Antioxidative effect of purple corn extracts during storage of mayonnaise

Chun-Ying Li, Hee-Woong Kim, He Li, Deug-Chan Lee, Hae-Ik Rhee

Abstract

Anthocyanin is a powerful natural antioxidant. Purple corn husk is rich in anthocyanin. In this paper the antioxidative effect of anthocyanin-rich purple corn husk extract (PCHE) in mayonnaise during storage was studied. The antioxidative effect of the mayonnaise containing PCHE was evaluated by measuring peroxide values, p-anisidine values, total oxidation values, acid values, and iodine values at time intervals for 10 weeks. The antioxidative effect of the mayonnaise containing PCHE was higher than that of mayonnaise with chemical antioxidants BHT and EDTA as positive control. The mayonnaise containing 0.4 g/kg PCHE showed the strongest antioxidative performance during storage. This study suggests that PCHE could be used as natural antioxidant in high fat food and as a substitute to chemical antioxidant with its purplish colour marking its difference from ordinary mayonnaise. Such colour difference will tell consumers that their food contains natural antioxidants.

1. Introduction

Mayonnaise is the most widely used sauces in the world today. Traditional mayonnaise is an oil-in-water (O/W) emulsion despite containing 70–80% fat and egg yolk (Dupree & Savage, 2001; Worrasonchai, Suphantharika, Pinjai, & Jammong, 2006). As with all high fat foods, mayonnaise is susceptible to deterioration due to autooxidation. Lipid oxidation of mayonnaise leads to reduction of storage generated by rancid order. Moreover, free radicals derived from lipid oxidation reactions are easily transferred to other molecules such as proteins, carbohydrates, and vitamins, especially in the presence of metals (Schaich, Kamal-Eldin, & Min, 2008). These oxidative attacks on food macromolecules contribute to the deterioration of flavour, aroma, colour, and nutritive value of food. In order to reduce and control lipid oxidation, antioxidants are added to foods. Synthetic antioxidants such as butylated hydroxytoluene (BHT), butylated hydroxy anisole (BHA), and ethylene diamine tetraacetic acid (EDTA) have been used in the food industry to prevent the oxidation of food fat. These products are more economical than natural antioxidant but also these products get a negative impression for being a chemical product. Plant materials rich in phenolic compounds have gained much attention because they exhibit a wide range of activities such as antioxidative, antimicrobial, anti-mutagenic, and anti-inflammatory activities (Kong, Chia, Goh, Chia, & Brouillard, 2003). Phenolic compounds act as antioxidants by donating electrons and terminating radical chain reactions (Tsuda, Shiga, Ohshima, & Kawakishi, 1996), as well as chelators by binding metal ions (Kähkönen, Hopia, & Heinonen, 2001). The antioxidative effects of natural plant materials rich in phenolics, such as extracts from berries (Heinonen, 2007), green tea (Almajano, Delgado, & Gordon, 2007), raisins (Williamson & Carugh, 2010), olives (Mattia, Sacchetti, Mastrocola, & Pittia, 2009), and grape seeds (Branann & Mah, 2007), have been tested in a variety of O/W emulsions. Research by Heinonen (2007) reported that anthocyanins isolated from black currants, raspberries, and lingonberries, as well as raspberry and blackberry juices, showed protection from lipid oxidation in O/W emulsions. In another study, olive polyphenols in O/W emulsions (Mattia et al., 2009), raisin extracts in O/W emulsions (Williamson & Carugh, 2010), and proanthocyanidin rich grape extracts in O/W emulsions (Branann & Mah, 2007) exhibited antioxidant activity toward lipid oxidation. The anthocyanins used as a food colourant in commercial production are mostly extracted from purple corn kernels, purple corn cobs, purple sweet potatoes, and blueberries (Kähkönen et al., 2001). Recently, we reported that purple corn husk contains...
approximately 10 times more anthocyanins (Li et al., 2008) than other anthocyanin producing plants (Cevallos-Casals & Cisneros-Zevallos, 2003; Jing, Noriega, Schwartz, & Giusti, 2007; Moreno, Hernández, & Velázquez, 2005). We can anticipate the industrial production of anthocyanin because purple corn husk contains 10% anthocyanin.

High-fat foods usually have been produced as O/W emulsion foods and frying foods. This study further investigated the antioxidative effects in stored mayonnaise as O/W emulsion food of anthocyanins extracted from purple corn husk.

2. Materials and methods

2.1. Materials

Purple corn husk extract (PCHE) (containing 20 g anthocyanin/100 g purple corn husk extract) was prepared and extracted from purple corn husk (2 kg) by using 75% ethanol for 16 h at room temperature in darkness and evaporating at 50 °C. The extracts were redissolved in 1% HCl/MeOH solvents, and their absorbance at 535 nm was measured to detect anthocyanin. Refined soybean oil, eggs, cider vinegar, and salt were purchased from a local market in Chuncheon, Korea. BHT, EDTA, and p-anisidine were purchased from Sigma (St., Louis, MO, USA). All other chemicals used were of analytical grade.

2.2. Preparation and storage of mayonnaise

Mayonnaise samples were prepared following the procedure developed in our previous work (Worrasinchai et al., 2006). Mayonnaise recipe contained the following ingredients in weight ratio (w/w): soybean oil (850 g/kg), egg yolk (72 g/kg), 8% cider vinegar (6 g/kg), and salt (72 g/kg). PCHE was added to the mayonnaise at anthocyanin concentrations of 0.1, 0.2, and 0.4 g/kg mayonnaise, which were referred to as PCHE 0.1, PCHE 0.2, and PCHE 0.4, respectively. BHT was added at concentrations of 0.1 g and 0.2 g/kg mayonnaise; EDTA was added at a concentration of 0.075 mg/kg mayonnaise. After preparation, the mayonnaise was filled in plastic commercial mayonnaise bags (700 ml) and sealed under vacuum. The bags of mayonnaise were stored at 4 °C and 25 °C in the dark, respectively, and sampling was performed at timed intervals.

2.3. Lipid extraction from mayonnaise

The mayonnaise was gently mixed prior to sampling. Thirty gram portions of mayonnaise were poured into 50 ml polypropylene centrifuge tubes. According to the procedure of Lagunes-Galvez, Cuvelier, Ordonnau, and Berset (2002), the samples were frozen at −20 °C for 24 h and thawed for 2 h at 4 °C to break the emulsion. Two milliliters of water were added and the mixtures were centrifuged at 4000 rpm for 20 min. The lipid phase separated from the emulsion residue was stored in closed glass flasks at −80 °C until analysed.

2.4. Oxidation experiments in mayonnaise

The progression of oxidation was monitored by determining peroxide values (POV), p-anisidine values (p-AV), total oxidation values (Totox V), acid values (AV), and iodine values (IV). AV and IV were determined using the method described by IUPAC (1987), and Totox V was calculated by a formula as reviewed by Rossell (1983): \[ \text{Totox V} = 2 \cdot \text{POV} + p\text{-AV} \]. The pigment patterns of the PCHE-added mayonnaise were analysed with extracts from the mayonnaise stored for 10 weeks using a UV-Vis spectrophotometer.

2.5. Statistical analysis

The data are reported as means ± SD for triplicate determinations. The analysis of variance and least significant difference tests (SPSS for Windows, Version Rel. 12.0, SPSS Inc., Chicago, IL) were conducted to identify differences among the means, while Pearson’s correlation test was carried out to determine the correlations among means. Statistical significance was declared at \( p < 0.05 \).

3. Results and discussion

Mayonnaise, similar to all high fat foods, is susceptible to spoilage due to auto-oxidation. Lipid oxidation has long been classified as the major form of deterioration affecting both the sensory and nutritional quality of food. Hydroperoxides are the primary oxidation products and are measured by means of peroxide values. In this study, antioxidants (BHT and EDTA) had significant (\( p < 0.05 \)) antioxidant effects on lipid oxidation in mayonnaise.

The POVs from the PCHE-added mayonnaise groups were significantly lower than those of the control, BHT 0.1, and EDTA groups from week 0 to 10 (Fig. 1A). In all samples, POV increased throughout storage at 25 °C from 0.6–0.7 meq/kg in week 0 to 4.3–13.6 meq/kg in week 10 (Fig. 1A). When compared to the negative control sample, initial POV developed similarly in all mayonnaise samples in week 0, but the POVs of the PCHE-added samples were significantly (\( p < 0.05 \)) lower than those in the negative control sample during the storage period. In week 10, the POV order of all mayonnaise samples was PCHE 0.4 < PCHE 0.2 < BHT 0.2 < PCHE 0.1 < BHT 0.1 < EDTA < control sample. With storage at 25 °C for 10 weeks, the PCHE 0.2 and PCHE 0.4 samples exhibited significantly (\( p < 0.05 \)) lower POVs (5.7 meq/kg and 4.3 meq/kg) and the control sample presented the highest POV (13.6 meq/kg). In all samples, POV ranges increased throughout storage at 4 °C from 0.6–0.7 meq/kg in week 0 to 0.8–1.5 meq/kg in week 10 (Fig. 1B). This trend was also observed in the samples stored at 25 °C. Mayonnaise samples stored at 4 °C, the differences between POVs were quite small and not statistically significant (\( p < 0.05 \)). In this study, antioxidants (BHT and EDTA) had significant (\( p < 0.05 \)) antioxidant effects on lipid oxidation in mayonnaise. The POVs of the PCHE-added mayonnaise groups stored for 10 weeks at 25 °C were reduced compared to the antioxidant (BHT and EDTA)-added mayonnaise samples. PCHE exhibited a significant antioxidant effect against primary oxidation in the mayonnaise groups. Many studies suggest that interactions between lipid hydroperoxides, the first products formed by oxidation, located at the droplet surface and...
transition metals from the aqueous phase are the most common cause of oxidative instability (Alamed, McClements, & Decker, 2006; McClements & Decker, 2000). The most likely decomposition is the decomposition of lipid hydroperoxides (ROOH) by peroxides into highly reactive peroxyl (ROO·) and alkoxyl (RO·) radicals, which react with unsaturated lipids within droplets or at the O/W interface, leading to the formation of lipid radicals. The lipid oxidation chain reaction propagates as these lipid radicals react with other lipids in their immediate vicinity (Abuja & Albertini, 2001). It was revealed that anthocyanins are able to donate a hydrogen atom to free radicals thus stopping the propagation chain reaction during lipid oxidation processes. On the other hand, EDTA was previously involved in metal-catalysing mechanisms in systems such as dressings and emulsions (Jacobsen et al., 2001; Let, Jacobsen, & Meyer, 2007). In the present study, the observed strong antioxidant activity of BHT suggests that free radical-scavengers reduced lipid oxidation in mayonnaise, which indicates that the initiation of lipid oxidation by existing free radicals might be an important factor. Therefore, taken together, it might be possible to further reduce oxidation by a combination of antioxidants having both free radical-scavenging and metal-chelating properties (Horn, Nielsen, & Jacobsen, 2009). Anthocyanins possess the powerful capacity of antioxidation with both free radical scavenging (Espin, Soler-Rivas, Wichers, & Garcia-Viguera, 2000) and metal-chelating properties (Nam et al., 2006). In the samples kept at 4 °C, POVs were significantly reduced, which must be ascribed to the fact that lipid oxidation was very slow in this case. The POVs of the mayonnaise samples stored at 4 °C had similar variation trends to the samples stored at 25 °C. The effectiveness of anthocyanins depends not only on their structural features but also on many other factors such as characteristics of the lipid system, temperature, and binding of the fatty acids (Yanishlieva-Masljarova, 2001).

Hydroperoxides are primary oxidation products and are unstable compounds that produce a number of secondary products such as alkanes, alcohols, aldehydes, and acids, some of which smell badly at low threshold values. The decomposition of hydroperoxides into secondary oxidation products is more closely related to flavour deterioration than hydroperoxide formation (Osborn & Akoh, 2003). Thus, when evaluating antioxidants, it is important to measure secondary and total oxidation before drawing conclusions on their efficacy and mechanisms of action. In this study, antioxidants were significantly (p < 0.05) affected with secondary oxidation and total oxidation in mayonnaise during the storage period.

The p-AVs of all samples increased throughout storage at 25 °C from 2.9–3.0 in week 0 to 4.9–8.8 in week 10 (Fig. 2A). In all mayonnaise samples at week 10, the order of p-AV was comparable to that for POV, and the PCHE-added samples had significantly lower scores than the control sample during the storage period. All samples stored at 4 °C had significantly lower scores compared to those at 25 °C, and the p-AV range of all samples was 3.4–5.3 in week 10 (Fig. 2B). Oxidation stability of the mayonnaise increased during storage as the amount of added PCHE increased, and the mayonnaise samples with PCHE 0.2 exhibited stronger oxidative stability effects than those with synthesized antioxidants (i.e., BHT), chemical chelating agents (i.e., EDTA).

Fig. 3 illustrates the effects of temperature and time on the Totox Vs. of the mayonnaise samples. Because Totox V is generated from POV and p-AV, a similar trend was observed when observing the Totox Vs. Throughout storage at 25 °C, Totox Vs. increased from 4.0–4.3 in week 0 to 13.1–36.0 in week 10 (Fig. 3A), and throughout storage at 4 °C, values increased from 4.0–4.3 in week 0 to 5.0–8.3 in week 10 (Fig. 3B). In week 10, the Totox Vs. reached maximal values at 36.0 for the control sample, and 13.1, 16.3, 19.5, and 32.0 for the other mayonnaise samples prepared using PCHE 0.4, PCHE 0.2, BHT 0.2, and EDTA, respectively, at 25 °C. As expected, the Totox Vs. of samples stored at 4 °C were lower than those stored at 25 °C in the different groups. The PCHE-added mayonnaise samples indicated lower Totox Vs. than their positive control samples such as BHT added at the same concentration and the EDTA-added mayonnaise. PCHE significantly (p < 0.05) reduced p-AV and Totox V were compared to the antioxidant (BHT and EDTA) and control samples over the entire storage period at both 4 °C and 25 °C. PCHE was more stable at 4 °C and less stable at 25 °C, and acted as an antioxidant in the mayonnaise due to its ability to scavenge radicals and chelating iron.

Acid values are a measure of the amount of carboxylic acid groups in a chemical compound, such as fatty acids, or in a mixture of compounds. AVs changed from 1.1 in week 0 to 1.5 in week 10 throughout storage at 4 °C (Fig. 4B) but there was no significant (p < 0.05) increase. However, in week 10, the AV of the control sample increased from 1.1 mg KOh/g lipid before storage to a maximal value of 2.2 mg KOh/g lipid and the samples prepared using PCHE 0.4, PCHE 0.2, BHT 0.2, and EDTA showed 1.5, 1.6, 1.6, and 1.9 mg KOh/g lipid, respectively, at 25 °C (Fig. 4A).

As another measurement index of lipid oxidation reaction, iodine values were determined in the mayonnaise samples after 0 and 10 weeks of storage at 25 °C, and are shown in Fig. 5A. IVs decreased throughout storage at 25 °C from 136 in week 0 to 49–110
samples demonstrated significantly higher values than the control and the samples with 160 added BHT and EDTA. Fig. 5B shows the IVs of all samples stored at 4 °C, which were significantly higher than those of samples stored at 25 °C. AV is the mass of potassium hydroxide in milligrams that is required to neutralize one gram of chemical substance. AV is a measure of the amount of carboxylic acid groups in a chemical compound, such as a fatty acid, or in a mixture of compounds. As oil-fats become rancid, triglycerides are converted into fatty acids and glycerol, causing an increase in AV. The PCHE-added mayonnaise samples had significantly (p < 0.05) lower AVs than the control samples over the entire storage period. Thus, PCHE appears to inhibit the oxidation processes of lipids in mayonnaise. As another measurement index of lipid oxidation reaction, IVs were determined in the mayonnaise samples. The PCHE-added groups had significantly higher IVs than the control. One application of the IV is for determination of the amount of unsaturation contained in fatty acids. This unsaturation is in the form of double bonds that react with iodine compounds. The higher the IV, the more unsaturated the fatty acid bonds that is present in a lipid, giving it more oxidation potential. However, the unsaturated fatty acids in the control sample were reduced because more unsaturated fatty acids were oxidised in this study (see Fig. 6).

In conclusion, PCHE, which is rich in anthocyanins, possesses good antioxidative activity in mayonnaise, and can be used as a natural antioxidant for mayonnaise products. Hence, natural anti-oxidants are valuable to increase the shelf-life of foodstuffs and provide protection to mayonnaise, replacing synthetic antioxidants such as BHT and EDTA.

Acknowledgements

This study was carried out with the support of the On-Site Cooperative Research Project (Project No. 20070201080023), RDA, Republic of Korea.

References


