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Effects of various coatings and antioxidants on peel browning of 'Bartlett' pears

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Abstract: Peel browning of 'Bartlett' pears (*Pyrus communis* L) caused by various mechanical injuries during postharvest handling results in a reduction in visual quality. Various commercial and experimental coatings and antioxidants with potential to reduce peel browning of pears have been evaluated. Treatment with 0.2% diphenylamine (DPA) or 0.3% ethoxyquin (Eth) reduced peel browning on 'Bartlett' pears induced by vibration, rolling or scuffing. However, this effect only lasted for about 5 days when treated pears were stored at 0 °C. For the consideration of practical use, pears would have to be treated and packed shortly before transport to achieve a reduction in peel browning. DPA and Eth did not reduce peel browning on pears induced by handling at 20 °C after treatment. It is suggested that tight-fill packaging and use of DPA or Eth would best reduce peel browning.

Keywords: *Pyrus communis*; diphenylamine; ethoxyquin; mechanical damage

INTRODUCTION

'Bartlett' pears (*Pyrus communis* L) are the leading pear variety produced in the USA and approximately 55% of the total US crop is produced in California. Fresh 'Bartlett' pears in the retail market often show peel browning. Peel browning of 'Bartlett' pears decreases the visual appeal of the fruit. This browning problem is a major source of customer dissatisfaction for this fruit.[1,2] Peel browning is caused by various mechanical injuries that occur during harvest, packing, transportation and marketing. Scuffing and abrasion on pear peel and impact bruising on pear flesh cause browning.[3]

The extent of browning depends not only on the severity of mechanical injury but also on the inherent browning potential of the fruits. Browning potential depends on the magnitude of polyphenol oxidase (PPO, EC 1.14.18.1) enzyme activity and the content of total phenolics.[4] In intact tissue, phenolic compounds are normally separated from the PPO enzyme and browning does not occur. However, when the fruit tissue is damaged, the PPO enzyme gains access to the phenolic compounds and catalyses enzymic browning. The browning process involves the oxidation of phenolic compounds to form quinones, which are very unstable and polymerise rapidly to form brown-coloured products.[5,6]

There are two strategies that can be employed to deal with the problem of peel browning of pears. As damage to fruit tissues leads to browning, preventing mechanical injury is an important method to avoid the occurrence of browning in fruit tissue.[7,8] Fruit coatings have the potential to reduce abrasion injury. However, it is often not possible to avoid all mechanical injury during postharvest handling of pears. In addition to preventing mechanical damage, the other strategy is to use an antioxidant. Treatment with antioxidant solutions may be able to prevent the browning action even when mechanical injury and mixing of PPO and phenolics have occurred.[2,4]

Commercially available and experimental coatings and antioxidants were tested for their potential to reduce peel browning of 'Bartlett' pears induced by mechanical injuries.

MATERIALS AND METHODS

Fruit materials

Commercially packed boxes of size 110 'Bartlett' pears were collected during the 2001 and 2002 commercial harvest seasons from local packinghouses in Lake County, CA, USA. Pears were transported on the day of harvest to the Pomology Postharvest Laboratory, University of California, Davis CA, USA and stored at −1 °C until used (no more than 2 weeks).

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Peel-browning induction methods

Four methods were employed to induce mechanical injuries to pear peel: vibration, rolling, scuffing and hand-handling. For the vibration method, pears were vibrated at 3.5–4 Hz with $1.1 \times g$ for 0.5 h at 0 °C. This was a simulation of the mechanical injury of pears caused by refrigerated truck transportation from the west coast to the east coast of the USA.[7,9] A vibration system was established to provide an accurate vibration level so that uniform vibration treatments could be inflicted among different experimental lots. Vibration on the tabletop was created by the vibration generator. The tabletop moved only in the vertical direction. The linkage connecting the tabletop to the motor was designed so that there was no vibration in the horizontal plane. Vibration intensity was controlled by adjusting the DC speed controller (model 4Z226E, Dayton Electric Mfg Co, Nilbs, IL, USA). The signal of vibration intensity was detected by a vibration sensor (an accelerator) and transferred to an AF 601 bandpass filter, and the vibration frequency was monitored by a multi-counter (John Fluke Mfg Co, Everett, WA, USA). Required vibration was achieved by adjusting the DC speed controller.

Peel-browning induction methods of rolling, scuffing and hand-handling were developed to confirm the efficacy for effective treatments. The rolling method involved rolling the pears individually down a 60 cm long × 12 cm wide × 8 cm high wooden slot held at a 25° angle with the ground. The surface of the slot was lined with medium-grit emery cloth. Each fruit was rolled down twice. Scuffing was done by dragging each fruit once for 50 cm over a coarse wooden surface using a uniform force. Hand-handling was done by rubbing the surface of each fruit 10 times uniformly with two hands. This method was to simulate peel browning potentially caused by consumers when fruits are displayed for sale in the market.

Evaluation of induced peel browning

Peel browning induced by mechanical vibration, rolling and hand-handling was judged both by the surface area browned and by the brown colour intensity in this area. Browning area was recorded as a percentage of the fruit surface, and brown colour intensity was determined on a 1-to-5 scale, where 1 = light brown and 5 = very dark brown. The amount and severity of pear peel browning were expressed by an index, which was calculated by the following formula:

$$\text{peel-browning index} = [(A \times 1 + B \times 2 + C \times 3 + D \times 4 + E \times 5) \times 0.75 + F \times 0.25]/\text{total \# fruits}$$

where, A = # pears with <1% brown area, B = # pears with 1–2% brown area, C = # pears with 3–5% brown area, D = # pears with 6–10% brown area, E = # pears with >10% brown area and F = total value of brown colour intensity for all pears evaluated.

Peel browning induced by scuffing on pears was evaluated by the brown colour intensity and subjectively recorded on a 1-to-5 scale, where 1 = light brown and 5 = very dark brown. The arithmetic mean of the colour intensity for all pears was used to express the magnitude of peel browning induced by scuffing.

Peel browning needs some time to be visible after induction. The time used was different with different peel browning induction methods. Peel browning induced on firm pears by hand-handling usually required 1 h to be visible. Vibration-induced peel browning normally took 24 h to be obviously visible when vibrated pears were held at 0 °C. The different evaluation times are shown in Table 1.

Flesh firmness and peel colour

Flesh firmness was determined with an automated fruit texture analyser using a 0.79 cm probe (GUSS Manufacturing (Pty) Ltd, Strand, Western Cape, South Africa). Peel was removed on two sides of the opposite equatorial region of each pear and firmness was measured on each side. External peel colour on opposite sides of each fruit was measured with a chromameter (model CR-300, Minolta, Ramsey, NJ, USA) in CIE $L^*a^*b^*$ mode. Changes in hue angle ($h°$), calculated as $h° = \tan^{-1}(b^*/a^*)$, were used to indicate the colour change from green to yellow during ripening (green ≈116°, yellow ≈98°).

Treatment with coatings and antioxidants

The effects of the following compounds and combinations of compounds on development of peel browning caused by mechanical injuries were evaluated: ethoxyquin (Eth, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline) (Decco Agrichemical Division, Atochem North America Inc, Monrovia, CA, USA), diphenylamine (DPA) (Pace International LLC, Seattle, WA, USA), 2-mercaptobenzothiazole (Sigma Chemical Co, St Louis, MO, USA), cysteine (Ajinomoto Co, Inc, Tokyo, Japan), NatureSeal (Mantrose-Haeuser Co, Inc, Westport, CT, USA), SemperFresh (AgriCoat Industries Ltd, Great Shefford, Berkshire, UK), 4-hexylresorcinol (Aldrich Chemical Company, Inc, Milwaukee, WI, USA), calcium lactate (Fisher Scientific, Fair Lawn, NJ, USA),

Table 1. Methods of peel-browning induction and evaluation for effective treatments

Browning induction method	Storage temperature (°C)		Time after induction for browning examination	Number of pears evaluated
	Before induction	After induction		
Vibration	0	0	24 h	3 boxes
Scuffing	0	0	10 min	30 pears
Rolling	0	20	1 h	30 pears
Hand-handling	0	0	24 h	30 pears
	20	20	1 h	30 pears

ascorbic acid (Fisher Scientific), sodium bisulphite (Sigma Chemical Co) and a combination of 2% ascorbic acid, 1% calcium lactate and 0.5% cysteine (pH 7). Concentrations tested are shown in Table 2.

For treatment with antioxidants, three boxes of pears were unpacked, warmed to room temperature (20–24 °C) and dipped into a solution containing the antioxidant for 5 min at room temperature. For treatment with coatings (NatureSeal and SemperFresh), three boxes of pears were unpacked, warmed to room temperature and dipped into a solution containing the antioxidant for 30 s at room temperature, and excess wax was wiped off with cheesecloth or paper. The treated pears were then dried with electrical fans, repacked tightly in the original box and placed at 0 °C overnight. Each box was subjected to vibration the following day at 3.5–4 Hz with $1.1 \times g$ for 0.5 h at 0 °C and then stored at the same temperature. Peel browning induced by this artificial vibration method was examined 24 h after vibration. In one experiment, vibrated pears were stored at 0 °C for 3 days and the pears were further vibrated a second time. The further vibrated pears were stored again at 0 °C and the effect of the compounds on the second vibration was checked 24 h later.

For treatments that were most effective in initial tests, treated pears were stored at 0 °C for up to 9 days and three boxes were vibrated on days 1, 5 and 9 during storage, and the peel browning was examined the following day. Peel browning was also induced by rolling, scuffing or hand-handling on an additional 30 pears (three replications of 10 pears each) on the same days (Table 1).

Statistical analysis

Analysis of variance (ANOVA) and Duncan's multiple range test (DMRT) were performed on all data using SAS statistical software (Version 7, SAS Institute Inc, Cary, NC, USA). Only data significant at $P < 0.05$ are discussed in the context.

Table 2. Compounds tested for their effects on peel browning of 'Bartlett' pears

Compound	Concentrations used
Eth	0.2, 0.25, 0.3%
DPA	0.05, 0.1, 0.15, 0.2%
2-Mercaptobenzothiazole	2, 3, 4% (in 60% ethanol solution)
NatureSeal	50, 75, 100%
Cysteine	0.5, 1%,
SemperFresh	1.0, 1.3, 2.0%
4-Hexylresorcinol	0.005, 0.01, 0.03, 0.05, 0.07, 0.1%
Ascorbic acid	1, 2, 4%
Calcium lactate	0.5, 1, 2%
Sodium bisulphite	2, 4, 6%
Combination	2% ascorbic acid, 1% calcium lactate, 0.5% cysteine (pH 7)

RESULTS

Evaluation of commercial and experimental treatments for potential to reduce peel browning

In the 2001 season, several possible methods to control peel browning of pears, including application of coatings containing antioxidants or of antioxidants alone, were explored (data not shown). However, the results showed that not all of the compounds had an effect. Compounds that showed the greatest control of peel browning of pears in the 2001 season included DPA, Eth, cysteine and the combination of 2% ascorbic acid, 1% calcium lactate and 0.5% cysteine (pH 7). Based on the results of the tests in 2001, the effective treatments were further evaluated in the 2002 season.

As shown in Fig 1, all the compounds tested in 2002 showed some effect in reducing peel browning induced by vibration simulating mechanical injury of pears during truck transport across the USA.[7,9] However, none of the compounds tested completely prevented vibration-induced peel browning. Compared with the untreated control fruit, the tested compounds reduced the peel browning index by 3–15%. The most effective treatments were 0.2% DPA and 0.3% Eth. Each reduced the peel browning index by about 15%. When the same boxes of pears were vibrated for a second time after 3 days at 0 °C, peel browning greatly increased for all treatments. Nevertheless, the tested compounds had a similar effect (Fig 1). While the magnitude of reduction in peel browning index of other compounds decreased, DPA reduced peel browning by 20% while Eth reduced peel browning by 16% compared with the untreated control.

The effects of the compounds were further tested by rolling to induce peel browning. The results show that the compounds were also effective to some extent in reducing peel browning induced by rolling (Fig 2). The most effective compounds again were DPA and Eth. Compared with the control fruit, treatment with 0.2% DPA or 0.3% Eth reduced the browning index by approximately 10%.

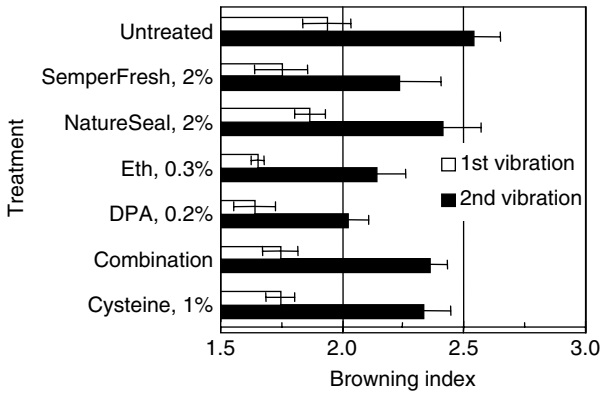

Figure 1. Effects of various compounds on peel browning of 'Bartlett' pears induced by vibration at 0 °C. Second vibration occurred 3 days after first one. Combination was a treatment with 2% ascorbic acid, 1% calcium lactate and 0.5% cysteine (pH 7).

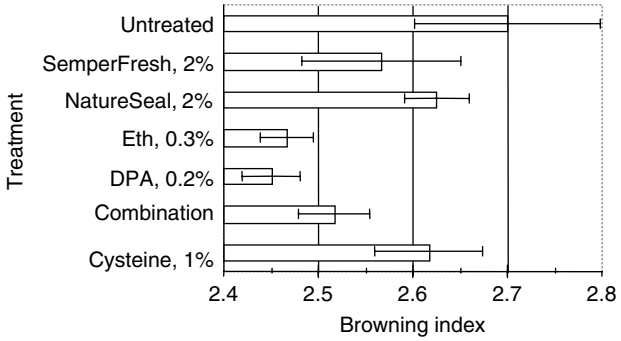

Figure 2. Effects of various compounds on peel browning of 'Bartlett' pears induced by rolling at 20 °C. Combination was a treatment with 2% ascorbic acid, 1% calcium lactate and 0.5% cysteine (pH 7).

To further confirm their efficacy, 0.2% DPA and 0.3% Eth were applied in a further experiment. A combination of 0.2% DPA and 0.3% Eth was tested. Similar results were obtained (Fig 3). Compared with the control fruit, treatment with 0.2% DPA or 0.3% Eth reduced the browning index by about 24%. However, the combination of 0.2% DPA and 0.3% Eth did not enhance the control of peel browning induced by vibration.

Longevity of anti-browning effects of DPA and Eth during cold storage

To investigate how long the anti-browning effect of DPA and Eth is retained during storage at 0 or 20 °C, pears treated with 0.2% DPA or 0.3% Eth were stored at 0 or 20 °C after treatment. For pears stored at 0 °C, browning was induced by vibration, scuffing or hand-handling. For pears stored at 20 °C, browning was only induced by hand-handling after 1, 5 and 9 days of storage.

When pears stored at 0 °C were vibrated in a tight-fill box, the effect of DPA and Eth lasted for about 5 days (Fig 4A). However, compared with the untreated control, the reduction in browning index changed from about 25% on day 1 after treatment to about 15% on day 5 after treatment. On day 9 after treatment, no difference in browning index between untreated control and treated pears was detected (Fig 4A). Similar results were obtained when pears treated with DPA or Eth were then inflicted with scuffing to induce peel browning (Fig 4B).

When DPA- or Eth-treated pears were stored at 0 °C before being inflicted with hand-handling,

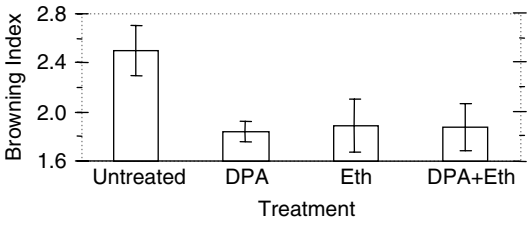

Figure 3. Confirmation of effects of 0.2% diphenylamine (DPA) and 0.3% ethoxyquin (Eth) on peel browning of 'Bartlett' pears induced by vibration at 0 °C.

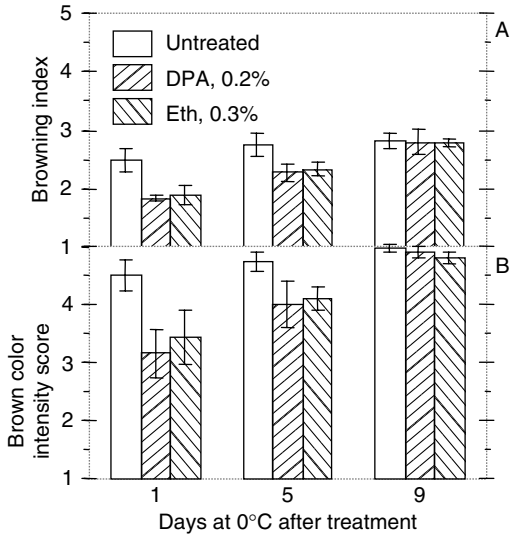

Figure 4. Effects of 0.2% diphenylamine (DPA) and 0.3% ethoxyquin (Eth) on peel browning of 'Bartlett' pears induced by vibration (A) or scuffing (B) at 0 °C after various days of storage at 0 °C after treatment. Treatments were applied prior to cold storage and damage was inflicted after storage.

the reduction in peel-browning index was about 23 and 14% after 1 and 5 days respectively in storage after treatment compared with the untreated control. However, almost no effect was observed when pears were held at 20 °C for as little as 1 day after treatment before handling.

Effect of DPA and Eth on fruit firmness and colour change of 'Bartlett' pears

No differences were found in fruit firmness or peel colour between DPA- or Eth-treated pears and untreated control fruit held at either 0 or 20 °C after treatment (data not shown). These results indicated that treatment with DPA or Eth did not influence the ripening process of pears.

DISCUSSION

Previous studies have shown that peel browning of pears can be reduced by application of antioxidants or coatings.[2,4,10] In our experiments, those reported to be effective in previous studies, such as 2-mercaptobenzothiazole,[11] 4-hexylresorcinol[12] and sodium bisulphite,[2,13] were not found to be effective, although concentrations higher and lower than the effective concentration previously reported were tested (Table 2). Serious phytotoxicity was observed when pears were treated with 4-hexylresorcinol even though the concentration applied was as low as 0.01% (data not shown). However, 2-mercaptobenzothiazole was used in 'd'Anjou' pears[11] while 4-hexylresorcinol was used in fresh-cut pears.[12] In addition, many factors, including genetic, agronomic and postharvest, influence the potential of pear browning.[4,14] All these factors could cause the results with the same compound on different pears to be different.

NatureSeal is a polysaccharide-based edible film with cellulose as the main component. SemperFresh is composed of sucrose esters of fatty acids, sodium carboxymethyl cellulose and mono/diglycerides of fatty acids. Both of them were reported to be effective to delay fruit ripening, keep fruit quality and increase shelf life.[15,16] Our results indicated that neither coating provided control of peel browning of 'Bartlett' pears (Figs 1 and 2). The combination of 2% ascorbic acid, 1% calcium lactate and 0.5% cysteine (pH 7) was reported to be effective to prevent pear browning.[17] However, our results showed that their effect in preventing peel browning of 'Bartlett' pears was variable. We and others have shown that use of only one component of the combination, ie ascorbic acid,[2] calcium lactate[12] or cysteine[18] (Table 2), did not reduce peel browning.

DPA and Eth are widely used in apples and Eth in pears for control of storage scald. Concentrations of 0.2% DPA or 0.27% Eth are commonly applied to ensure maximum scald control.[19] Scald is, in fact, an oxidative peel-browning disorder of apples and pears that develops during storage. Treatment with DPA or Eth is considered the most effective way to control scald.[2,20,21] Our results consistently show that treatment with 0.2% DPA or 0.3% Eth reduced peel browning on 'Bartlett' pears induced by vibration (Figs 1 and 3), rolling (Fig 2) or scuffing (Fig 4B). However, this effect was retained for only about 5 days when treated pears were stored at 0 °C (Figs 4A and 4B). This means that, in practice, pears should be treated and packed immediately before transport to see any reduction in peel browning.

The effect of DPA and Eth was not found to be additive (Fig 3). The reason for this is possibly because DPA and Eth function in a similar manner as an antioxidant in the tissue. However, this hypothesis needs to be further proved experimentally. In addition, cell disruption (bruises, wounding, tissue lysis) leading to loss of compartmentalisation involves a cascade of events, including the activation of latent PPO and/or systemic *de novo* induction of PPO.[4] When the effect of DPA and Eth declines, peel browning will occur possibly because of the induction of new PPO. This may be another reason why the effect of DPA and Eth was not additive and why peel browning cannot be controlled completely by treatment with DPA and/or Eth. Our results show that neither DPA nor Eth kept their longevity of anti-browning efficacy for more than 5 days when treated pears were held at 0 °C (Figs 4A and 4B). Therefore peel browning caused by newly synthesised PPO 5 days after treatment could not be controlled by treatment with DPA or Eth alone, or their combination.

Temperature may influence the effect of DPA and Eth. Our results show that DPA and Eth did not reduce peel browning on pears handled during ripening at 20 °C after treatment, but they did when pears inflicted with hand-handling were held at 0 °C. One of the reasons for this could be that at the higher temperature the effect of DPA and Eth wore off more rapidly. In addition, peel browning needed some time to be obviously visible after browning induction. Symptoms of peel browning induced by hand-handling developed much more quickly at 20 than at 0 °C. The elapsed time between browning induction and evaluation of damage may influence the judgement of the magnitude of peel browning. It was observed that hand-handling induced peel browning was not fully visible in less than 24 h when damaged pears were held at 0 °C after induction. Therefore, while evaluation of the hand-handling-induced peel browning was conducted 1 h after handling for pears held at 20 °C, evaluation for pears held at 0 °C was conducted 24 h after induction (Table 1). If evaluation for pears held at 0 °C had been conducted in less than 24 h after browning induction, there may have been no differences in peel browning between DPA- or Eth-treated pears, and untreated control pears, as the symptoms of peel browning had not yet fully developed.

It was also observed that 'Bartlett' pears were not sensitive to hand-handling-induced peel browning when fruit firmness was higher than about 30 N. However, when fruit firmness was lower than 30 N, their susceptibility to hand-handling increased so greatly that no difference in peel browning between treated and untreated pears could be observed. At 20 °C, fruit softening was much quicker than for fruit held at 0 °C. Firmness decreased to 30 N at 20 °C in 3–5 days. This is possibly another reason why peel browning on ripening pears induced by handling cannot be reduced by treatment with DPA or Eth before ripening the fruit at 20 °C.

DPA, the simplest secondary aromatic amine, may cause some pear fruit phytotoxicity. Rizk *et al*[22] reported considerable pear fruit phytotoxicity when DPA was used for controlling scald in 'Le Conte' pears. Eth was found to be a good scald control agent and did not cause injury to pear fruit.[2] No phytotoxicity was encountered in our experiments, indicating that the concentration of DPA used in our experiments may be below the level to cause any phytotoxicity in 'Bartlett' pears, or that susceptibility to phytotoxicity is variable.

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