# Fate of Apple Peel Phenolics during Cool Storage

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Consumption of certain phenolics in the diet is considered beneficial to human health. In this study, individual phenolics were measured by diode-array HPLC at monthly intervals in the peel of Granny Smith, Lady Williams, and Crofton apple cultivars stored in air at 0 °C for 9 months. The concentrations of total phenolics significantly differed among the cultivars examined, with Lady Williams peel having significantly more phenolics (over 4000 $\mu g \cdot g^{-1}$ peel fresh weight) than Crofton (2668 $\mu g \cdot g^{-1}$ peel fresh weight) and Granny Smith, which had the lowest concentration of total phenolics (1275 $\mu g \cdot g^{-1}$ peel fresh weight). There were also significant differences in individual phenolics among cultivars and during storage. Quercetin glycosides were the only flavonols identified, with quercetin rhamnoglucoside being the most abundant phenolic in the peel. Chlorogenic acid was the major cinnamic acid derivative, with high concentrations, up to 412 $\mu g \cdot g^{-1}$ peel fresh weight, in Crofton peel. A pre-storage diphenylamine (DPA) treatment had few significant effects on peel phenolic metabolism. Where differences did occur, fruit treated with DPA retained higher concentrations of total peel phenolics during storage than fruit not treated with DPA. Storage of all cultivars for up to 9 months in air at 0 °C induced few significant changes in the peel phenolic concentrations. This indicates that phenolic metabolism in apple peel is relatively stable, and the health benefits of phenolics in apple peel should be maintained during long-term storage.

**Keywords:** *Malus spp.; phenolics; storage; peel; DPA*

## INTRODUCTION

Phenolics are an important class of compounds that are derived from phenylalanine via the shikimate and phenylpropanoid pathways (*1*) and are widely found in apple peel (*2*). The major classes of phenolics in apple peel include phenolic acids (hydroxybenzoic acids, hydroxycinnamic acids (chlorogenic acid)); and the flavonoids, e.g., flavans, (catechin), procyanidins (condensed tannins), flavonols (quercetin glycosides), chalcones (phloretin glycoside), and anthocyanins (cyanidin glycosides) (*1*−*3*). These compounds have numerous important roles in the human diet (*4*), with a major one being their significant antioxidant potential (*5*). For example, apple phenolics have been shown to inhibit the oxidation of low-density lipoprotein, which is widely considered to be a pivotal event in the development of atherosclerosis (*6*). In addition, apple phenolics have been found to inhibit the proliferation of human tumor cells in vitro (*7*).

The role of phenolics in the fruit is unclear, but they may play an important part in the physiology and metabolism in the apple peel. For example, phenolics act as substrates for browning enzymes (*8*) and are important antioxidants (*9*). In addition, phenolics are an important aspect of fruit quality (*1*) and have also been implicated in pathogen resistance and some physiological disorders (*10*, *11*).

Because of the increased interest in apple peel phenolics in the diet, it is important to obtain reliable data on the identity, concentration, and fate of these compounds in various cultivars. In addition, many apples eaten by consumers have been stored for up to 9 months and there is little information on the effect of storage on the fate of peel phenolics.

Phenolic metabolism is a complex process, as phenolics undergo constant turnover and degradation (*12*, *13*). It is therefore important to document and understand their metabolism during long-term storage. There have been relatively few studies that examined the fate of apple fruit phenolics during storage and even fewer that have examined peel phenolics. Awad and de Jager (*14*) recently measured the levels of chlorogenic acid and flavonoids in the peel of Jonagold and Elstar apple cultivars, and showed that these compounds were relatively stable during both regular air storage and controlled-atmosphere storage.

Unfortunately, much of the early literature regarding apple fruit phenolics is inconsistent and unreliable because of uncertainties in identification and quantification. The development and availability of new techniques, such as diode-array HPLC, $^{1}H$ nuclear magnetic resonance (NMR), $^{13}C$ NMR, and fast-atom bombardment mass spectroscopy (FABMS), has now enabled a more reliable and accurate identification of apple phenolics.

This paper describes the extraction, identification, and quantification of phenolics in apple peel and their fate during cold storage in air at 0 °C in three apple

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10.1021/jf0015266 CCC: $20.00 
Published on Web 04/12/2001

cultivars: Granny Smith, Lady Williams, and Crofton. The post-storage effects of diphenylamine (DPA) treatment on the fate of peel phenolics in Granny Smith and Lady Williams apples were also investigated. DPA is a well-known antioxidant that is a common commercial treatment for the control of the physiological storage disorder superficial scald. DPA also has numerous effects on apple physiology (*15*), and its effects on peel phenolic metabolism are not known.

## MATERIALS AND METHODS

**Source of Fruit.** Preclimacteric Granny Smith and Crofton cv. apples were harvested from a commercial orchard at Orange, New South Wales. Preclimacteric Lady Williams apples were harvested at Harcourt, Victoria, and transported overnight. After harvest, half of the Granny Smith and Lady Williams apples were dipped in diphenylamine (14.7 mM $l^{-1}$ Shield-Brite Division, Pace International, Seattle, WA). Four replicates of each cultivar and treatment were stored in regular air storage in plastic-lined boxes at 0 °C for up to nine months.

At monthly intervals, 10 apples from each replicate were removed from storage and a representative sample of the peel (50 g) was carefully removed with an apple peeler. Excess parenchyma tissue was scraped from the peel tissue before the peel was frozen in liquid nitrogen, ground, and stored (−75 °C) for later analysis.

**Quantitative Extraction.** Apple peel (2 g) samples were extracted with methanol (80%, 10 mL) containing naringenin (25 $\mu g \cdot mL^{-1}$) as an internal standard. The peel was sonicated for 20 min, then centrifuged at 4000*g* for 10 min. The extract was passed through a C-18 Sep-Pak column (Waters, Milford, MA; Millipore, Bedford, MA) to remove unwanted waxes and chlorophyll.

**Analytical HPLC.** A Hewlett-Packard 1090 HPLC system with diode-array detection was used to separate and quantify the apple peel phenolics. A C-18 column (ODS-2, 250 mm, Spherisorb) was maintained at 40 °C during analysis. The solvent program used A (0.1% trifluroactetic acid in water) and B (0.1% TFA in acetonitrile) as the mobile phase, with a flow rate of 1 mL $min^{-1}$. The solvents were regularly sparged with helium. The column was equilibrated with 10% acetonitrile and held for 5 min following injection of 20 $\mu$L of sample. The acetonitrile was then increased from 10% to 20% over 35 min. A second gradient from 20% to 50% acetonitrile over 5 min completed the run. The phenolics were detected using a diode-array detector (from 200 to 400 nm) but were monitored at 254 and 280 nm.

**Quantification.** The phenolics were classified into their appropriate phenolic classes (e.g., hydroxycinnamic acid derivatives, flavonols, etc). To quantify the phenolics using the internal standard, naringenin, the relative response factor for each phenolic class was calculated, using a representative phenolic from each class. The individual procyanidins (procyanidin B2, B5, and trimer) were identified by retention time and UV spectra and quantified from individual procyanidin standards. The linearity of the relative response of each of the standard phenolics was examined over the range of concentrations observed in apple peel. Samples (20 $\mu$L) of 6.25−100 $\mu$g phenolic standard$\cdot mL^{-1}$ in 80% methanol were injected into the analytical C-18 column using the standard analytical HPLC method and relative responses for each phenolic standard were determined.

| phenolic class | standard phenolic used for quantification |
|---|---|
| dihydrochalcone | phloridzin |
| flavan-3-ol | epicatechin |
| flavonol | quercetin rhamnoglucoside |
| hydroxycinnamic acid | chlorogenic acid |

**Reference Compounds.** Caffeic acid, catechin, chlorogenic acid, coumaric acid, epicatechin, ferulic acid, naringenin, phloridzin, and quercetin rhamnoglucoside standards were purchased from Sigma-Aldrich (St. Louis, MO). Procyanidin B2, B5, and trimer, were quantified from individual procyanidin standards kindly provided by Dr. Jane Lancaster, New Zealand Institute for Crop and Food Research Limited, Christchurch, New Zealand.

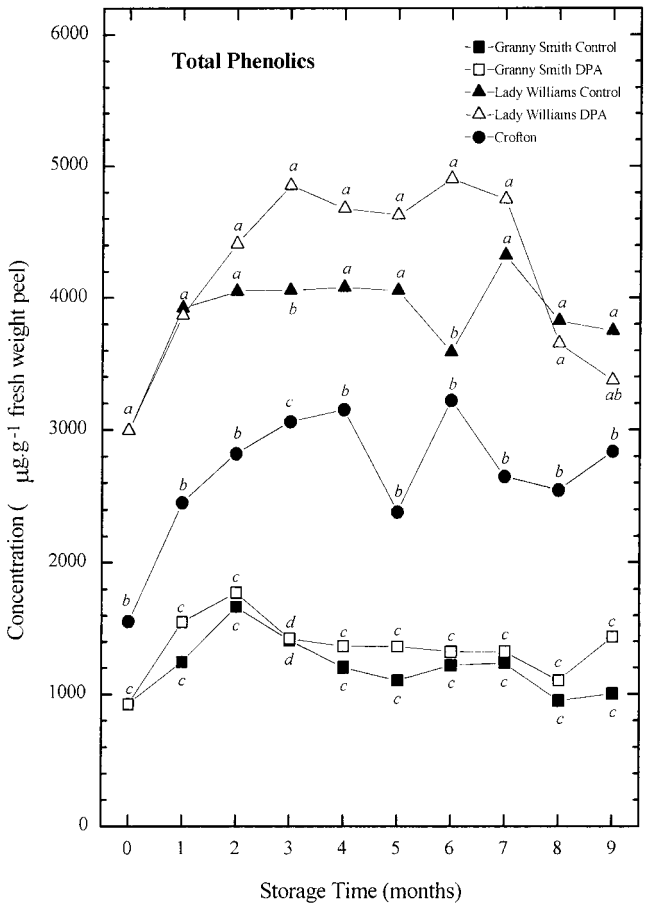


**Figure 1.** Concentrations of total phenolics ($\mu g \cdot g^{-1}$ fresh weight) in Granny Smith, Lady Williams, and Crofton apple peel during storage in air at 0 °C. DPA was applied to the treated samples of Granny Smith and Lady Williams apples before storage. Concentrations accompanied by different letters within each time differ significantly at $P < 0.05$.

## RESULTS AND DISCUSSION

There were significant differences in peel phenolic content among the cultivars examined. Over the storage period and across all treatments, the average concentration of total extractable phenolics in the peel of Lady Williams (4036 $\mu g \cdot g^{-1}$ fresh weight) was higher than that in Crofton (2668 $\mu g \cdot g^{-1}$ fresh weight) which was in turn higher than that in Granny Smith (1275 $\mu g \cdot g^{-1}$ fresh weight). In addition, the concentrations of extractable phenolics changed during the course of the storage period. In general, during storage in air at 0 °C, the concentrations of total extractable peel phenolics in all three cultivars increased during the first few months before remaining constant or slowly declining (Figure 1). This is consistent with the general observations of Burda et al. (*3*) who showed there were no great changes in the concentration of the major phenolics in the peel of Rhode Island Greening, Empire, and Golden Delicious cv. apples; where the concentrations remained relatively constant over a normal air storage period of six months. Coseteng and Lee (*2*) also showed, in nine other apple cultivars, that changes in phenolics over the initial 4 month storage period were minor.

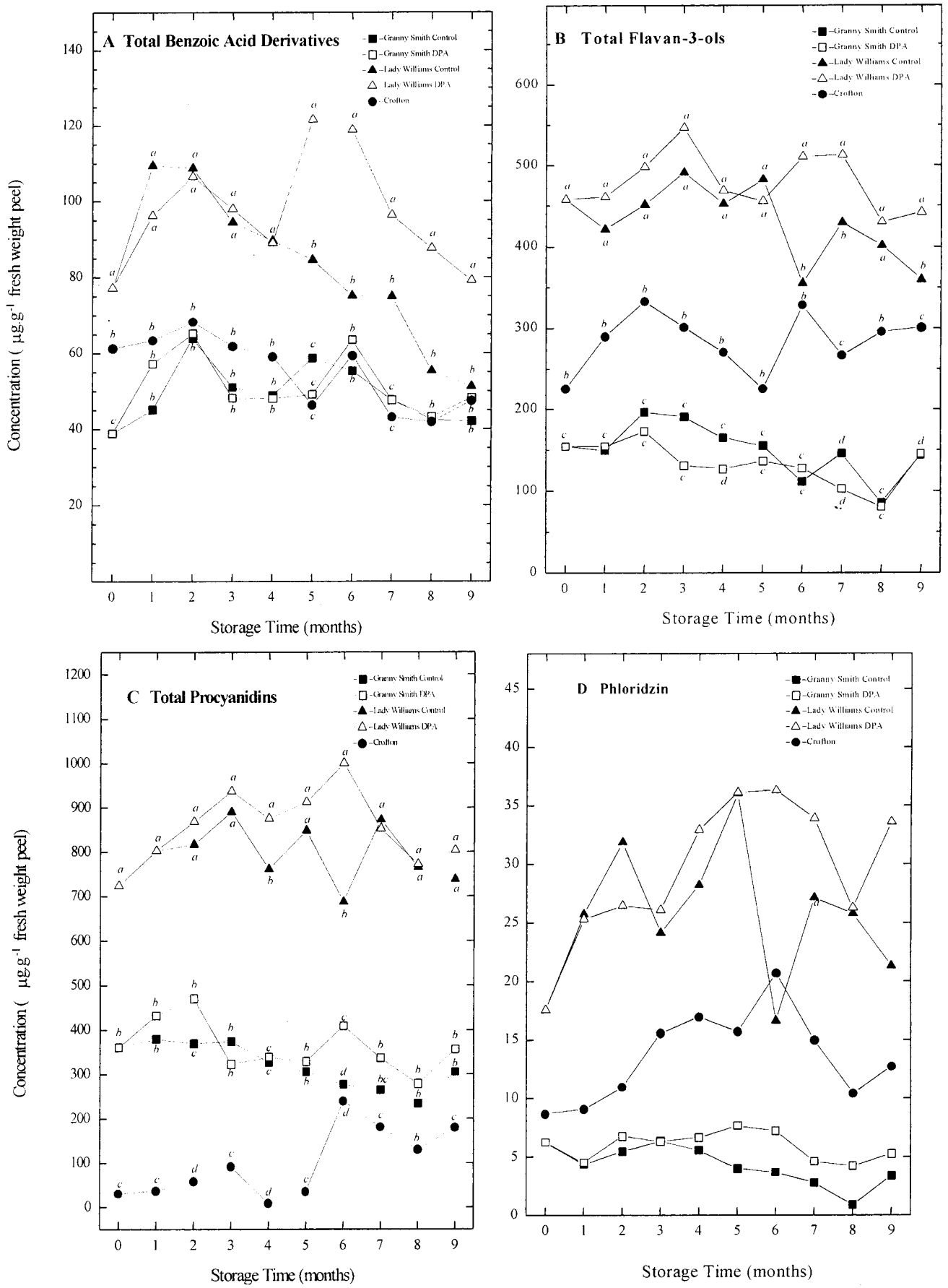


**Figure 2.** Concentrations of (a) total benzoic acid derivatives, (b) total flavan-3-ols, (c) total procyanidins, and (d) phloridzin ($\mu g \cdot g^{-1}$ fresh weight) in Granny Smith, Lady Williams, and Crofton apple peel during storage in air at 0 °C. DPA was applied to the treated samples of Granny Smith and Lady Williams apples before storage. Concentrations accompanied by different letters within each time differ significantly at $P < 0.05$.

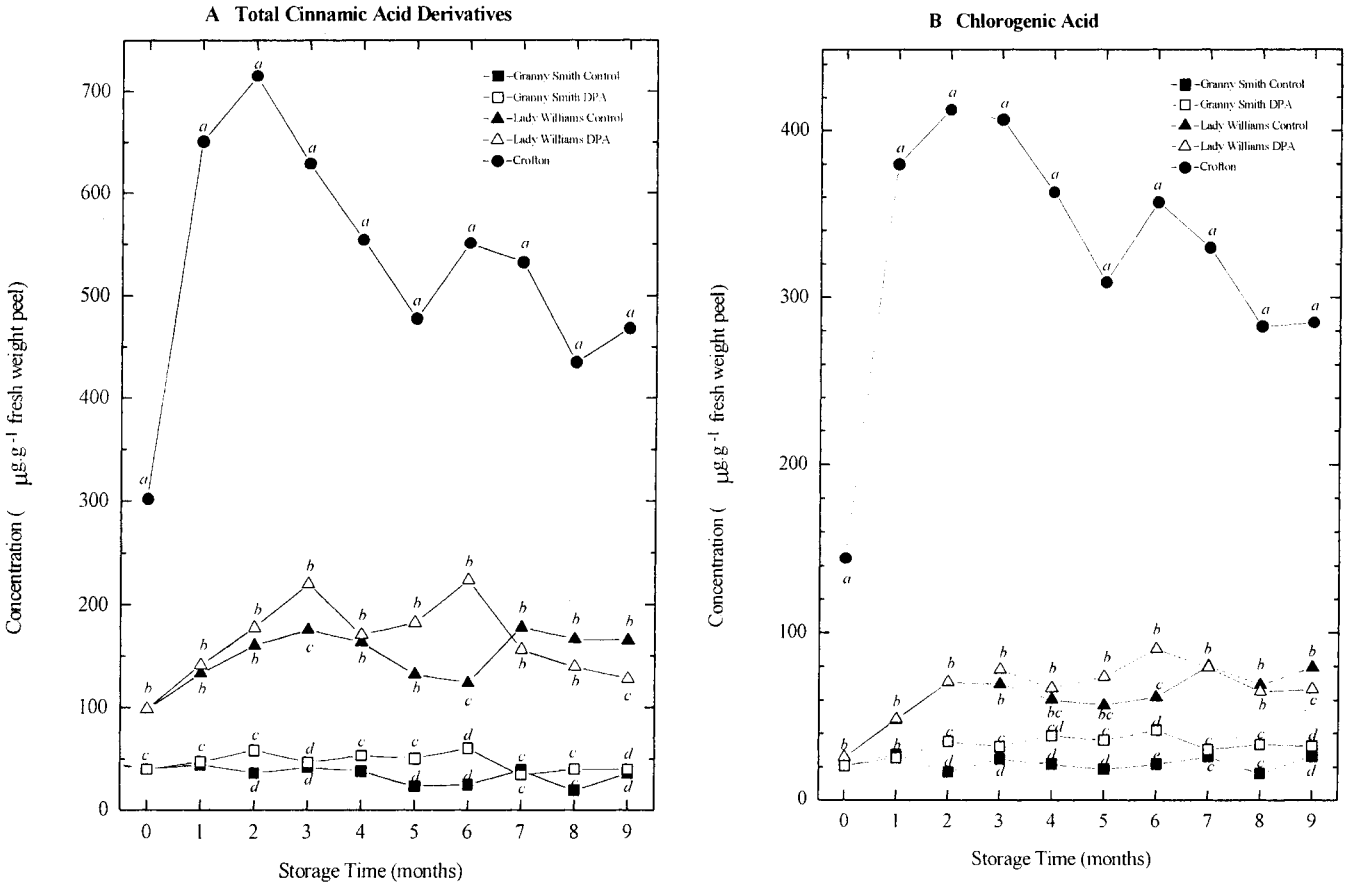


**Figure 3.** Concentrations of (a) total cinnamic acid derivatives and (b) chlorogenic acid ($\mu g \cdot g^{-1}$ fresh weight) in Granny Smith, Lady Williams, and Crofton apple peel during storage in air at 0 °C. DPA was applied to the treated samples of Granny Smith and Lady Williams apples before storage. Concentrations accompanied by different letters within each time differ significantly at $P < 0.05$.

The initial increase in peel phenolics observed in this study during the early stages of storage may coincide with the respiratory and ethylene climacteric in the apple fruit which initiates ripening (*16*−*18*). The first step of phenolic biosynthesis involves the production of trans-cinnamate from phenylalanine by phenylalanine ammonia lyase (PAL). Increased PAL activity and ethylene production have been shown to coincide with ripening in Red Delicious and Golden Delicious apples (*19*), and PAL activity has been shown to have a direct influence on total flavonoids in apples (*20*). Total phenylpropanoid metabolism has also been shown to be induced by ethylene (*21*, *22*). These observations may be relevant to phenolic turnover in climacteric fruit such as apple, and may help explain differential phenolic metabolism in apples during cold storage. However, the role of ethylene and ripening on phenolic metabolism has yet to be fully explored in apple peel.

Within the various classes of phenolics there were large differences in the quantities of peel phenolics. For example, the concentrations of total benzoic acid derivatives were low and variable, contributing less than 5% of total phenolics. Lady Williams peel contained significantly more total benzoic acid derivatives than the other cultivars, where benzoic acid derivatives increased for the first few months of storage then gradually declined (Figure 2a). By the end of the storage period these changes were not significant. In addition, there were few significant differences in the concentrations of total benzoic acid derivatives among cultivars and DPA treatment over the storage period.

Procyanidins have been recognized as an important component of total antioxidant potential of food (*23*). The concentrations of total procyanidins in the peel of Granny Smith and Lady Williams were generally higher than in Crofton (Figure 2c). The concentrations of total procyanidins in Granny Smith peel generally declined during the storage period, however in Lady Williams peel, after an initial increase in the levels of procyanidins, the concentrations of total procyanidins remained relatively constant during storage (Figure 2c). Similar to the findings of Burda et al. (*3*), procyanidin B2 and procyanidin trimer comprised a significant proportion of the total procyanidins, and their relative concentrations and trends over time were very similar to those of total procyanidins (data not shown). In this study procyanidin B5 was detected only in the peel of Lady Williams, but its concentration was significantly lower than that of the other procyanidins. In general, the concentrations of total procyanidins were higher in the peel of DPA-treated fruit than control fruit, however, these differences were not always significant.

The three cultivars contained significantly different concentrations of flavan-3-ols (catechin and epicatechin) across the entire storage period (Figure 2b). The concentrations of flavan-3-ols in the peel of Lady Williams were greater than those in Crofton, which in turn were higher than those in Granny Smith. The concentration of the catechin and epicatechin reflected the changes in total flavan-3ols, where the concentrations of epicatechin in the peel were approximately double those of catechin, and the concentration of catechin in Lady

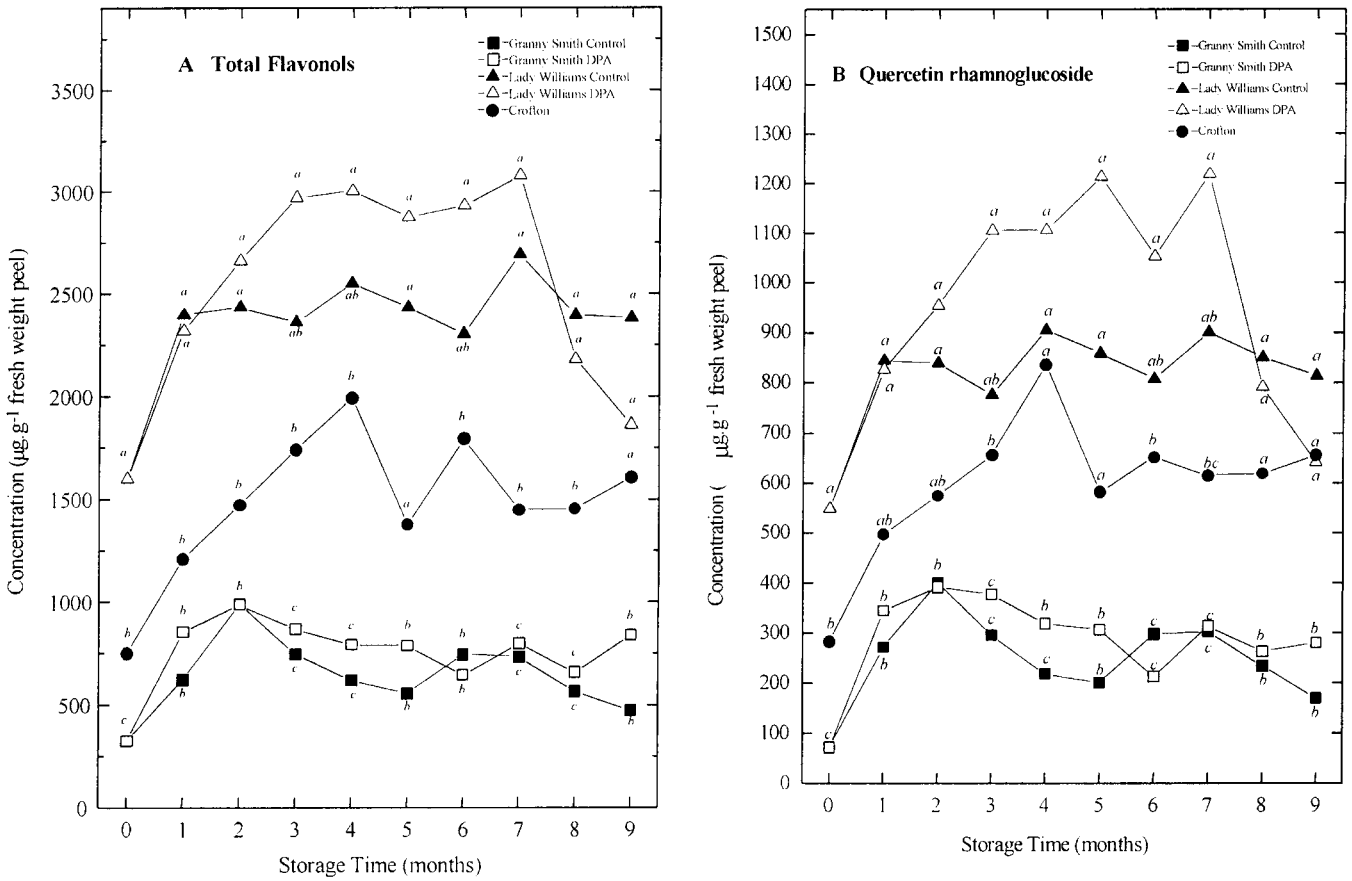


**Figure 4.** Concentrations of (a) total flavonols and (b) quercetin rhamnoglucoside ($\mu g \cdot g^{-1}$ fresh weight) in Granny Smith, Lady Williams, and Crofton apple peel during storage in air at 0 °C. DPA was applied to the treated samples of Granny Smith and Lady Williams apples before storage. Concentrations accompanied by different letters within each time differ significantly at $P < 0.05$.

Williams peel was about 3 times higher than that in Crofton and Granny Smith (data not shown). The concentration of total flavan-3-ols in all cultivars increased during the first few months of storage and then remained constant or declined during storage. Burda et al. (*3*) also found in the peel of Rhode Island Greening apples that there was also an initial rise in the levels of epicatechin during the first two months of storage followed by a decrease. For most of the storage period, there were few differences between the DPA-treated and control fruit within a cultivar.

Dihydrochalcones are characteristic of apples and their content can vary greatly depending on cultivar (*24*). Phloridzin was the only chalcone identified in the peel of apples and was present in relatively low concentrations: reaching of a maximum 35 $\mu g \cdot g^{-1}$ peel fresh weight (Figure 2d). Other phloretin glycosides, such as xylosylglucose have been identified in apple peel (*25*), but the very low concentration of unknown compounds in these samples meant that they were not identified in the fruit. Lady Williams peel always contained more phloridzin than Granny Smith, whereas the concentrations of phloridzin in Crofton peel were intermediate. DPA treatment had no significant effect on phloridzin concentrations.

Cinnamic acid derivatives are of particular interest in the human diet (*26*) and they significantly contribute to total phenolics in apple peel, and particularly chlorogenic acid in Crofton apples. In this study, all major cinnamic acid derivatives (caffeic acid, coumaric acid, chlorogenic acid, and ferulic acid) were identified in the apple peel, except sinapic acid, and no coumarins were identified. The total concentration of cinnamic acid derivatives in Crofton peaked at 2 months of storage, at which time the maximum concentrations of cinnamic acid derivatives were more than 4 and 12 times greater than those at the same storage time in Lady Williams and Granny Smith, respectively (Figure 3a). Indeed, the total concentrations of cinnamic acid derivatives in Crofton were always greater than in Lady Williams and Granny Smith apple peel. The concentration of total cinnamic acids remained relatively constant over the storage period in the peel of Granny Smith, but in Lady Williams the total concentrations of total cinnamic acids increased until 3 months. These results were similar to those reported by Costeng and Lee (*2*) in the 9 apple cultivars they examined over a 16-week period, but their results contrast with those of Mosel and Herrmann (*27*) who showed that the concentration of cinnamic acids consistently decreased in Schoner von Boskoop cv. apples during storage at 4 °C.

The high concentrations of total cinnamic acid derivatives in the peel of Crofton were mainly due to the high concentrations of chlorogenic acid (up to 412 $\mu g \cdot g^{-1}$ fresh weight). The general trends in the concentrations of chlorogenic acid were similar to those of the total cinnamic acid derivatives (Figure 3b). The concentrations of chlorogenic acid in Lady Williams and Granny Smith peel were relatively low, with a maximum of 80 $\mu g \cdot g^{-1}$ fresh weight in the peel of Lady Williams DPA after 6 months storage. These high concentrations of chlorogenic acid in apple peel may have significant

health benefits. For example, Clifford (*26*) concluded that the health benefits and metabolism of chlorogenic acid derivatives are diverse and there is great potential for their further utilization in the human diet. The observations in this study are inconsistent with other apple peel studies with different cultivars, in which the concentrations of chlorogenic acid in peel were similar (*3*), suggesting significant cultivar differences.

In this study, there were generally few differences in the concentrations of cinnamic acid derivatives and chlorogenic acid between the DPA-treated and control fruit of either cultivar. However, when significant differences did occur, the DPA-treated apples had more total cinnamic acid derivatives than the control fruit (Figure 3a,b). Changes in the concentration of caffeic acid and ferulic acid during storage were similar to the trends of chlorogenic acid, although the absolute concentrations were significantly lower, particularly in the peel of Crofton (data not shown).

Flavonols are an important source of antioxidant activity (*28*) and are an important component of the phenolic profile, comprising about 80% of the total extractable phenolics. The only flavonols in apple fruit are the quercetin glycosides: the concentrations in the peel of Lady Williams (maximum of about 3000 $\mu g \cdot g^{-1}$ fresh weight) were higher than those in Granny Smith (maximum 991 $\mu g \cdot g^{-1}$ fresh weight). The concentrations of flavonols in the peel of Crofton were intermediate (Figure 4a). The concentrations of total flavonols in the peel of all apples were affected by time and treatment (Figure 4a) and the trends in total flavonol concentration over the storage time were similar for all apple cultivars. The concentrations of total flavonols increased during the first 2−4 months of storage, and then either plateaued or slowly declined. This is reflected in the trends in the individual flavonols, which were dominated by quercetin rhamnoglucoside (Figure 4b). Quercetin rhamnoglucoside contributed around 30% of the total flavonols. Lady Williams had significantly higher concentrations of quercetin rhamnoglucoside than Granny Smith (Figure 4b). The concentrations of quercetin rhamnoglucoside in Crofton were higher than in Granny Smith; this difference became significant only after 3 months of storage. Quercetin glycosides were the only flavonols identified in the peel. The concentrations of the other quercetin glycosides (quercetin xyloside, quercetin galactoside, quercetin glucoside, quercetin arabinopyranoside, and quercetin arabinofuranoside) were present in lower concentrations and followed similar trends to quercetin rhamnoglucoside (data not shown). These glycosides were significantly higher in Lady Williams peel throughout the storage period. Quercetin arabinopyranoside was found only in relatively low concentrations in the peel of Lady Williams and was undetectable or present in low concentrations in Granny Smith or Crofton throughout storage (data not shown). Although DPA-treated fruit generally had higher concentrations of total flavonols (including quercetin rhamnoglucoside), these differences were not significant.

In other phenolic peel studies, the overall concentrations of total flavonols were variable and cultivar dependent (*3*, *29*). These observations show that the concentrations of phenolics vary widely among cultivars, and the qualitative differences among cultivars are small. However as mentioned previously, nonspecific bulk methods for the extraction, identification, and quantification of apple phenolics can often be misleading.

DPA is a common commercial postharvest treatment used during long-term storage to suppress the storage disorder superficial scald. Superficial scald is a serious physiological disorder that affects some susceptible apple cultivars, such as Granny Smith. Piretti et al. (*11*) demonstrated the involvement of phenolics in the development of scald. Although DPA is a well-known antioxidant that is widely used, its physiological effects and mode of action to prevent scald are unknown. In general, the concentrations of all phenolics (i.e., benzoic acid derivatives, cinnamic acid derivatives, flavan-3-ols, flavonols, and procyanidins) and consequently total phenolics in peel of stored fruit treated with DPA at harvest were higher than in the control (nontreated) peel. However these differences were not often statistically significant ($P < 0.05$). This suggests that the antioxidant DPA does not affect phenolic metabolism. This is in contrast to Duvenage and De Sward (*30*) who concluded that DPA inhibited both the synthesis and oxidation of flavonols during storage.

We conclude that, although peel phenolics vary among cultivars, they remain relatively stable during storage in air at 0 °C and indicate that peel phenolic metabolism and turnover are low during long-term storage.

## ACKNOWLEDGMENT

The individual procyanidins (procyanidin B2, B5 and trimer) were quantified from individual procyanidin standards kindly provided by Dr. Jane Lancaster, New Zealand Institute for Crop and Food Research Limited, Christchurch, New Zealand.

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Received for review December 27, 2000. Revised manuscript received March 7, 2001. Accepted March 7, 2001.

JF0015266