JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Cultivar and Growing Region Determine the Antioxidant Polyphenolic Concentration and Composition of Apples Grown in New Zealand

TONY K. MCGHIE,* MARTIN HUNT, AND LAURA E. BARNETT

The Horticulture and Food Research Institute of New Zealand Limited, Private Bag 11030, Palmerston North, New Zealand

Evidence suggests that increasing consumption of fruit and vegetables contributes to improved health and well-being by providing protection from diseases including various cancers and cardiovascular disease. Although there is uncertainty about which components generate this effect, an attractive hypothesis is that the antioxidants are at least partly responsible. We measured the polyphenolic concentrations in 10 different apple cultivars grown commercially in New Zealand, each sourced from three different geographic regions. Our results showed that the concentration of polyphenolics varied among the apple cultivars, with Pacific Queen containing 2.7 times the amount of polyphenolics found in Cox's Orange. Furthermore, there were significant differences in polyphenolic concentrations in fruit from different regions for some cultivars but not for others. We also measured the polyphenolic concentrations in apple skin and flesh and found that on average 46% of the polyphenolics in whole apples were in the skin. Essentially all of the flavonols (quercetin derivatives) were present in the skin. To maximize the intake of apple polyphenols, it is necessary to consume apples of cultivars with high polyphenolic concentrations such as Pacific Queen and include the skin. Our results also showed that there is potential for promoting apple fruit from specific geographical regions because they contained elevated concentrations of antioxidant polyphenolic compounds.

KEYWORDS: Apple; malus; flavonoids; anthocyanins; polyphenolics; antioxidants

INTRODUCTION

There is considerable evidence to show that a greater intake of fruit and vegetables contributes to improved health and well-being by reducing the risk of diseases such as cardiovascular disease and some forms of cancer (*1*−*4*). This evidence base has resulted in a recommendation to consume at least 5 servings (or 400 g) of fruit and vegetables per day (*5*). Although it is not known with any certainty which components of fruit and vegetables are responsible for this protective effect, it is thought that the antioxidant phytochemicals that they contain might be partly responsible (*6*). Fruits and vegetables contain many different antioxidant components (e.g., polyphenolics, vitamin C, carotenoids, vitamin E, and glucosinolates); however, the polyphenolic phytochemicals are potent antioxidants and represent a substantial portion of dietary antioxidants consumed.

Increased consumption of the major type of polyphenolics, the flavonoids, has been associated with reductions in coronary heart disease (*7, 8*). Apples are a major source of polyphenolics and flavonoids in the diet (*9*−*11*), and therefore represent a major source of dietary antioxidant. Apple consumption has been linked with a reduction in the risk of lung cancer, asthma, type-2 diabetes, thrombotic stroke, and ischemic heart disease (*7*).

Apples, in addition to containing high concentrations of antioxidant polyphenolic phytochemicals (*12*−*14*), also contain a large number of different types of polyphenolics, including flavonols (quercetin glycosides), cinnamic acids (chlorogenic and caffeic acids), flavanols (catechin, epicatechin, and polymeric proanthocyanins), dihydrochalcones (phloridzin), and anthocyanins (cyanidin glycosides) (*15, 16*). The polyphenolic content of apples also varies by cultivar (*17*−*19*), nutrient conditions (*20*), and location within the tree (*21*). Consequently, the antioxidant value of apple in the diet can vary substantially. The objective of this study was to provide a better understanding of the antioxidant value of apples by measuring the polyphenolic content of a selection of New Zealand grown apple cultivars and determining the influence of regions (with different climates).

MATERIALS AND METHODS

Study Design. A total of 10 apple cultivars currently grown commercially and available from three regions of New Zealand with different growing conditions were selected for this study. All apples were sourced from HortResearch's research orchards in Havelock North (Hawke's Bay), Riwaka (Nelson), and Clyde (Central Otago). The selected cultivars are listed in **Table 1**, and the climatic characteristics

* To whom correspondence should be addressed. Telephone: +64-6-356-8080 ext 7822. Fax: +64-6-351-7004/3546731. E-mail: tmcghie@hortresearch.co.nz.

10.1021/jf047832r CCC: $30.25
Published on Web 03/24/2005

Table 1. Descriptions, Mean Physical Dimensions, and Harvest Information of the Apple Cultivars Selected for This Study

cultivar	description	size (mm)	weight (g)	date of first harvest: Hawke's Bay	Nelson	Central Otago
Braeburn	orange/red bicolor comprising a color wash over 40% or more of the surface area with a bright orange/red fleck over the color wash	79	201	20 Mar	28 Mar	20 Mar
Cox's Orange	bicolor with an open red stripe covering 50% or more of the surface area or with a blush covering 20% or more of the surface area	72[a]	149	13 Feb	15 Feb	25 Feb
Granny Smith	block color green with dark to pale green skin color	78[a]	197	28 Mar	05 Apr	03 Apr
Pacific Beauty	bicolor with 50% or more coverage of block pink to bright red color	81	201	12 Feb	14 Feb	26 Feb
Pacific Queen	bicolor with 66% or more coverage of block bright red color	81[a]	205	13 Mar	22 Mar	11 Mar
Pacific Rose	bicolor with 50% or more coverage of bright rosy pink color	83	227	22 Mar	05 Apr	25 Mar
Pink Lady	bicolor with 40% or more coverage of bright pink blush color	79[a]	200	27 Mar	08 Apr	03 Apr
Red Delicious	bicolor to full color, with 60% or more covered by a red stripe on a red over color through to a solid block red appearance	76[a]	186	13 Mar	10 Mar	28 Mar
Royal Gala	bicolor with 50% or more coverage of a red blush overlain by a bold red fleck or stripe	75	175	13 Feb	21 Feb	25 Feb
Jazz	bicolor with a bright orange/red fleck over a red color wash covering 40% or more of the apple surface area	78[a]	184	17 Mar	21 Mar	14 Mar
mean		78.2	175	9 Mar	15 Mar	15 Mar

[a] Estimates. Because of a shortage of data for some cultivars, weight is a more accurate measure of fruit size.

Table 2. Location and General Characteristics of the Climatic Parameters for Each of the Regions from Which Fruit Were Collected[a]

	rainfall (mm)	sunshine (h)	mean temp. (°C)	max temp. (°C)	min temp. (°C)
Hawke's Bay 39° 39′, 176° 53′	798	2057	12.9	31.6	–4.6
Nelson 41° 7′, 172° 59′	1381	2372	12.5	29.3	–3.4
Central Otago 45° 12′, 169° 19′	360	2075	10.1	32.8	–8.9

[a] Data presented are from the period 1950–1980.

for each of the three regions are described in **Table 2**. A total of 20 fruit were selected from trees maintained under cultural and management conditions appropriate to the regions and were transported overnight to Palmerston North. Fruit were held at 2 °C until analysis but for not longer than 7 days.

Sample Preparation and Extraction. From the 20 apples collected for each sample, 15 were selected that were free of defects, and these were divided into three replicate groups of five apples. Four plugs (8 mm in diameter × 1.5 cm in length) were taken from the equator of each of the five apples at perpendicular locations. The skin was separated from the flesh with a scalpel blade. All 20 plugs from the 5 apples of a replicate group were combined and extracted as a single sample, as were all skin samples of each replicate group. To extract the polyphenols, 50 mL of ethanol/water/formic acid (80:20:1) was added to the plugs from five apples and homogenized using a UltraTurrex blender. The corresponding skin discs were cut in half before the addition of the solvent (5 mL) and homogenization with the UltraTurrex. Both skin and flesh samples were extracted at 4 °C for 24 h and centrifuged at 3000 rpm for 10 min. Extracts were stored at −20 °C until analyzed by reversed-phase HPLC.

Reversed-Phase HPLC Analysis. The HPLC system used consisted of a Waters Alliance 2690 HPLC equipped with a 996 photodiode array detector. The separation column was an Aqua 5μ C18 250 × 4.6 mm (Phenomenex, Torrance, CA) protected with a guard column of the same packing. The solvents used were (A) 5% formic acid in water and (B) 100% acetonitrile. The solvent program started at an initial composition of 95% A and 5% B, increasing to 50% A and 50% B at 35 min, and then 20% A and 80% B at 40 min. After a further 5 min, the system was reset to the starting composition for the next injection at 55 min. Sample injection volume was 5 μL. Chromatographic data were collected and manipulated using the Waters Millennium Chromatography Manager version 4.0. Spectral data were collected (250−600 nm, 2 nm resolution) for the entire run, and the polyphenolic components were quantified by extracting chromatograms at 280, 350, and 530 nm. Catechin, epicatechin, procyanidins, and phloridzin were quantified using chromatograms extracted at 280 nm; flavonoids and chlorogenic acids, at 350 nm; and anthocyanins, at 530 nm. External calibration curves were constructed for chlorogenic acid, epicatechin, quercetin-3-rutinoside, quercetin, cyanidin 3-*O*-galactoside, and phloridzin. Standards were purchased from Sigma (Sydney, Australia) except for cyanidin 3-*O*-galactoside, which was purchased from Polyphenols Laboratories (Sandes, Norway). Components for which standards were not available were quantified using the standard curve of a related compound. For example, all of the quercetin glycosides were quantified using the calibration curve for quercetin 3-rutinoside, and procyanidins were quantified using the calibration curve for epicatechin. Total phenolics were determined by taking the sum of all peaks detected between 7 and 18 min and quantified using the epicatechin calibration curve. Total procyanidin concentrations were determined by summing the total peak area in the 280 nm chromatogram between 10 and 20 min and subtracting known nonprocyanidin components (e.g., chlorogenic acid and epicatechin). The resulting peak area was quantified using the epicatechin calibration curve. Statistical analysis was performed using GenStat for Windows version 7 (VSN International, U.K.). Differences were assessed using the Tukey multiple comparison procedure; a p value of less than 0.05 was considered significant.

RESULTS

The physical characteristics of the apple cultivars and the climatic parameters for each growing location selected for this study are shown in **Tables 1** and **2**, respectively. The apple cultivars selected represent the main cultivars currently grown in New Zealand, with Braeburn, Pacific Rose, and Royal Gala accounting for approximately 75% of the total production. The other apple cultivars are grown in much lower volumes, and several of these apple cultivars are recent releases (e.g., Jazz), and are not yet well-known in international markets. The three growing regions, Hawke's Bay, Nelson, and Central Otago, represent the main apple-producing regions of New Zealand.

Apples contain a substantial number of different phenolic compounds (*18*, *22*). The concentrations and types of poly-

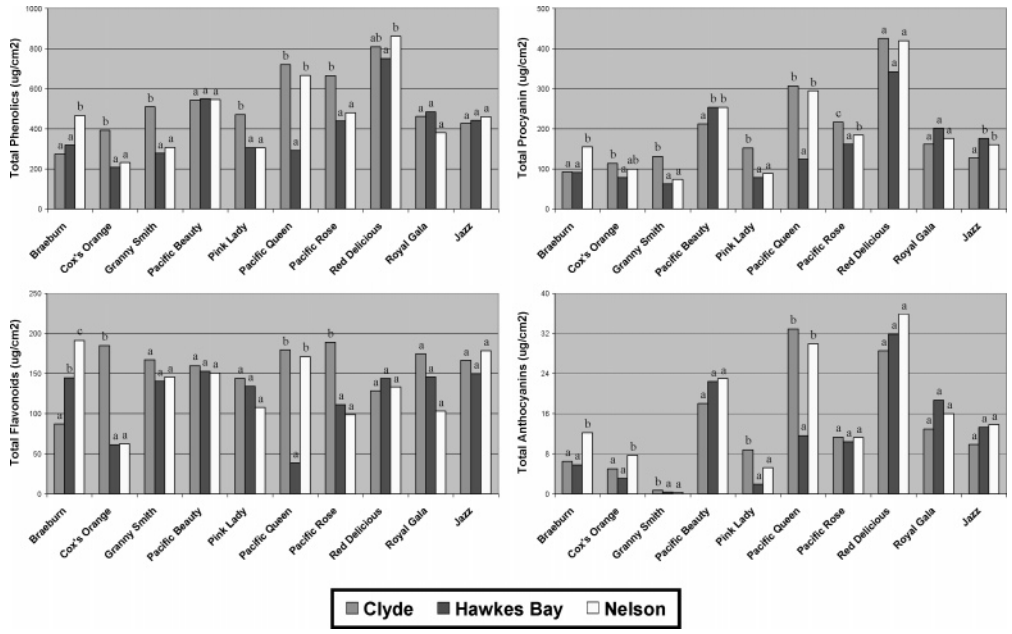

Figure 1. Concentrations of total phenolics, total flavonols, total procyanidins, and total anthocyanins found in the skin of the 10 apple cultivars from each geographic region. Values for each region with the same letter were not significantly different for each cultivar at the 5% significance level (Tukey test).

phenolic compounds detected in the apple cultivars investigated in this study were similar to previous studies (*17*, *19*) and included flavonols (quercetin 3-rutinoside, quercetin 3-galactoside, quercetin 3-glucoside, quercetin 3-xyloside, quercetin 3-arabinosidef, quercetin 3-arabinosidepy, and quercetin 3-rhamnoside), cinnamic acids (chlorogenic acid), dihydrochalcone (phloridzin); flavanols (catechin and epicatechin), anthocyanins (cyanidin 3-galactoside), and procyanidins. The concentrations of the totals phenolics, flavonoids, and procyanidins are shown in **Figure 1** (skin) and **Figure 2** (flesh) for each of the cultivars from each growing region. The numerical values for total phenolic concentrations are given in **Table 3** and show the variation for each cultivar grown in the different regions for both the skin and flesh portions of the fruit. For flesh, the total phenolic concentration tends to be higher in fruit from Clyde (Central Otago) for Granny Smith, Pacific Beauty, Pink Lady, Pacific Queen, and Pacific Rose but similar for fruit from all three regions for Braeburn, Cox's Orange, Red Delicious, Royal Gala, and Jazz. In contrast, skin total phenolic concentrations showed much less variation with fruit of Pacific Beauty, Red Delicious, Royal Gala, and Jazz from all growing regions having similar concentrations. Thus, growing regions did influence phenolic composition, but the amount of the difference was highly cultivar-dependent. The difference between the lowest and highest for the different polyphenolic compounds in the cultivars of this study ranges from 3.1 times for flavonoids in flesh to 15.1 times for procyanidins in skin (**Table 4**).

Apples are frequently consumed as a whole fruit; therefore, to compare the differences between cultivars, the physical data for each cultivar were used to calculate the amount of polyphenolic in an average apple for each cultivar; these data are shown in **Table 5**. On the basis of the total polyphenolic contents as mg/apple, the 10 apple cultivars can be divided into three groups with Braeburn and Cox's Orange in the low group, Granny Smith, Royal Gala, Pink Lady, and Jazz in the medium group, and Pacific Beauty, Pacific Rose, Red Delicious, and Pacific Queen in the high group.

The method used for sampling the fruit allowed the effective separation of the skin layer from the underlying flesh cells; therefore, we have reported the polyphenolic concentrations for both the skin and flesh separately. In **Table 6**, the polyphenolic

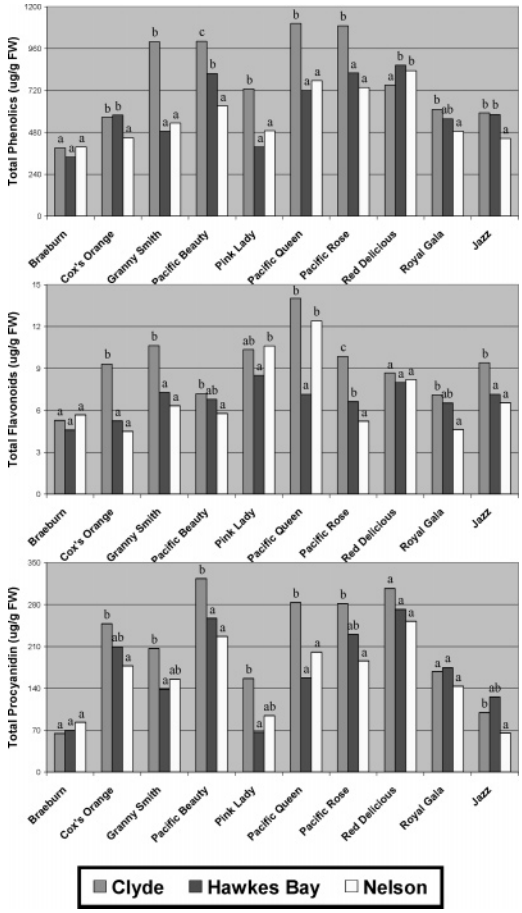

Figure 2. Concentrations of total phenolics, total flavonols, and total procyanidins found in the flesh of the 10 apple cultivars from each geographic region. Values for each region with the same letter were not significantly different for each cultivar at the 5% significance level (Tukey test).

Table 3. Total Phenolic Concentrations Measured in the Skin and Flesh for Each Apple Cultivar[a]

	total phenolics							
	skin (μg/cm^2)				flesh (μg/g FW)			
	Hawke's Bay	Nelson	Central Otago	mean	Hawke's Bay	Nelson	Central Otago	mean
Braeburn	319	467	274	348	337	395	388	368
Cox's Orange	208	231	392	277	578	448	565	530
Granny Smith	278	307	510	330	485	533	998	597
Pacific Beauty	550	546	543	546	816	630	1001	815
Pacific Queen	292	666	720	612	719	775	1103	895
Pacific Rose	439	479	665	500	819	735	1089	840
Pink Lady	306	305	471	376	395	489	728	564
Red Delicious	750	861	808	806	864	832	750	815
Royal Gala	484	380	461	441	556	485	610	550
Jazz	442	460	427	443	582	444	590	544
mean	423	539	543	497	590	579	752	638

[a] Total phenolic concentrations were calculated by combining the areas of all of the HLPC peaks eluting between 7 and 18 min and the epicatechin calibration curve.

Table 4. Comparison of the Minimum and Maximum Concentrations of Polyphenolics and the Cultivar/Regional Origin

compound	min (cultivar/location)	max (cultivar/location)	factor difference
	Skin (μg/cm^2)		
total phenolics	208 (Cox/Hawke's Bay)	861 (Red Delicious/Nelson)	4.1
total flavonoids	39 (Pacific Queen/Hawke's Bay)	189 (Pacific Rose/Central Otago)	4.8
total procyanidins	6.1 (Pacific Queen/Hawke's Bay)	92.4 (Red Delicious/Nelson)	15.1
phloridzin	1.9 (Cox/Hawke's Bay)	25.7 (Red Delicious/Nelson)	13.5
chlorogenic acid	8.6 (Cox/Nelson)	51.0 (Pacific Queen/Central Otago)	5.9
flavanols	25.2 (Braeburn/Hawke's Bay)	92.3 (Pacific Rose/Central Otago)	3.7
	Flesh (μg/g FW)		
total phenolics	337 (Braeburn/Hawke's Bay)	1103 (Pacific Queen/Central Otago)	3.3
total flavonoids	4.5 (Cox/Nelson)	14.0 (Pacific Queen/Central Otago)	3.1
total procyanidins	64.4 (Braeburn/Central Otago)	306.9 (Red Delicious/Central Otago)	4.8
phloridzin	3.2 (Cox/Nelson)	31.4 (Red Delicious/Nelson)	9.8
chlorogenic acid	50 (Cox/Central Otago)	420 (Pacific Queen/Central Otago)	8.4
flavanols	61 (Jazz/Nelson)	242 (Pacific Rose/Central Otago)	4.0

Table 5. Total Polyphenolic Amounts Calculated on a Per Fruit Basis Including Both Skin and Flesh Contributions[a]

cultivar	total flavanols (mg/apple)	total flavonols (mg/apple)	phloridzin (mg/apple)	total procyanidin (mg/apple)	chlorogenic acid (mg/apple)	anthocyanin (mg/apple)	total phenolics (mg/apple)
Cox's Orange	20.2	17.7	1.0	47.4	10.6	0.9	97.7
Braeburn	19.6	28.8	2.3	36.0	20.7	1.5	109.1
Granny Smith	36.9	29.6	1.5	45.6	27.6	0.1	141.4
Royal Gala	24.3	26.0	1.7	60.1	27.6	2.8	142.5
Pink Lady	29.6	27.7	1.8	44.7	43.7	1.0	148.5
Jazz	21.2	32.6	1.6	47.2	51.4	2.6	156.6
Pacific Beauty	48.0	33.1	3.0	103.5	18.4	4.8	210.8
Pacific Rose	55.8	27.9	2.3	89.8	54.7	2.4	232.8
Red Delicious	43.5	26.1	9.3	123.3	34.5	6.5	243.2
Pacific Queen	40.7	33.0	2.6	100.8	80.3	5.7	263.1

[a] The flesh contribution was calculated by multiplying the flesh concentrations as μg/g by the average weight for their respective cultivar, whereas the skin contribution was calculated by multiplying the skin concentrations as μg/cm^2 by the surface area of the respective cultivar.

concentrations have been calculated on a whole apple basis and displayed as the percentage in the skin and flesh. Some polyphenolic components are found predominantly in the skin, for example, anthocyanins and flavonol (quercetin glycosides), whereas others such as chlorogenic acid, phloridzin, epicatechin, and procyanidin are present in both the skin and flesh.

DISCUSSION

The results of this study showed that apple cultivars differ significantly in both the total and individual concentrations of antioxidant polyphenolic components. Because apples are often consumed on a whole fruit basis, we calculated the amount of polyphenolic consumed per apple. In terms of total polyphenolics, the apple cultivar with the greatest polyphenolic content (Pacific Queen) contained 2.7 times more polyphenolics than the lowest cultivar (Cox's Orange) (**Table 5**). These results indicate that apple polyphenols consumption can be increased simply through appropriate cultivar choice.

The polyphenolic content of some apple cultivars also varied significantly depending on the region in which they were grown. For example, polyphenolic concentrations in the cultivars Pacific Beauty, Pacific Queen, Pacific Rose, and Granny Smith showed significant variation between regions, whereas for cultivars such as Braeburn, Royal Gala, Jazz, and Red Delicious, variation was not significant. In the cultivars that showed the greatest variation, fruit from Clyde (Central Otago) often but not always contained the greatest polyphenolic concentration. For example, the skin of Pacific Queen from Central Otago had 2.5 times

Table 6. Relative Amounts of Polyphenolics Present in Skin and Flesh of the 10 Apple Cultivars Included in This Study

	flavanols		flavanols		phloridzin		procyanidin		chlorogenic acid		anthocyanin		total polyphenolics	
cultivar	skin (%)	flesh (%)	skin (%)	flesh (%)	skin (%)	flesh (%)	skin (%)	flesh (%)	skin (%)	flesh (%)	skin (%)	flesh (%)	skin (%)	flesh (%)
Cox's Orange	25	75	95	5	43	57	33	67	16	84	100		42	58
Braeburn	30	70	96	4	40	60	60	40	11	89	100		55	45
Granny Smith	20	80	95	5	37	63	33	67	11	89	100		38	62
Royal Gala	32	68	96	4	43	57	53	47	10	90	100		50	50
Pink Lady	29	71	93	7	51	49	49	51	12	88	100		43	57
Jazz	36	64	96	4	42	58	61	39	10	90	100		48	52
Pacific Beauty	27	73	96	4	46	54	48	52	15	85	100		49	51
Pacific Rose	27	73	95	5	47	53	44	56	13	87	100		39	61
Red Delicious	34	66	94	6	42	58	58	42	14	86	100		52	48
Pacific Queen	33	67	93	7	63	37	54	46	11	89	100		43	57
mean	29	71	95	5	45	55	50	50	12	88	100		46	54

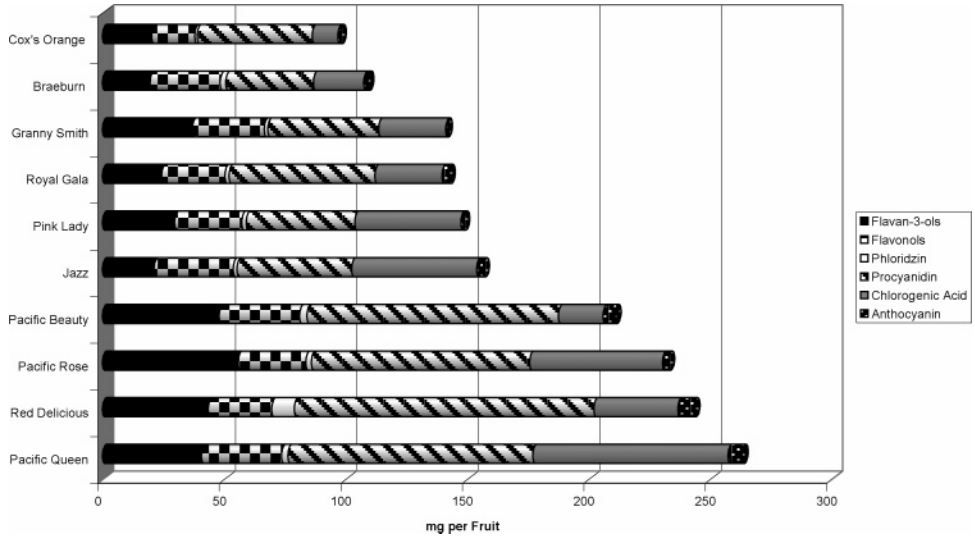

Figure 3. Cumulative sum and relative composition of each type of polyphenol expressed on a per apple basis.

the concentrations of total polyphenolics than skin of Pacific Queen from Hawke's Bay. The reasons for this difference in polyphenolic concentrations are unknown, although increased pigments (anthocyanins) in apple skin are often attributed to combinations of low overnight temperatures and high levels of sunshine hours during ripening (*23*). However, most of the polyphenolics in apple skin are nonanthocyaninic in nature. Furthermore, polyphenolics were also elevated in the flesh of some apple cultivars from Central Otago. For example, the polyphenolic content of Granny Smith apples from Central Otago was 2.1 times and 1.9 times higher than those of Granny Smith apples from Hawke's Bay and Nelson, respectively. Therefore, the difference observed in certain cultivars between the regions appeared to affect the polyphenolic content of the whole apple. The results of this study show that an environmental effect that varies between growing regions had a substantial effect on polyphenolic content of some apple cultivars but not others. The environmental factors causing this or the reasons why some cultivars but not others are apparently susceptible are not known.

Not only did the total polyphenolic concentration vary between cultivars, but apples contain a large number of individual polyphenolic compounds and these also varied between cultivar. The average polyphenolic composition for the different apple cultivars investigated in this study from all three growing regions is presented in **Figure 3**. Quantitatively, both anthocyanins and phloridzin are minor phenolic components of apple, whereas flavan-3-ols (catechin and epicatechin), procyanidins, and chlorogenic acid constitute the majority of the polyphenolics. The amount of flavonols (quercetin glycosides) is relatively consistent between the different cultivars, but the proportion of the total changes substantially.

Increased consumption of fruit and vegetables is widely promoted because of a association with positive benefits to health and well-being. The World Health Organization has recommended that people consume at least 5 servings or 400 g of fruit and vegetables per day to reduce the risk for cardiovascular diseases and some forms of cancers (*5*). Polyphenolic compounds, such as cinnamic acids and flavonoids have substantial antioxidant activity (*24*, *25*), and their concentrations are positively correlated with antioxidant activity of fruit (*26*), including apples (*13*). Furthermore, epidemiological studies have shown relationships between apple consumption and a reduction risk for a number of chronic diseases (*7*). Therefore, it seems reasonable to believe that an increased consumption of apple polyphenolics may be beneficial to health and well-being. Increased consumption of apple polyphenols is possible by simply increasing the amount of apple consumed. However, the results of this study show that it is equally feasible to increase the consumption of apple polyphenols by substituting apple cultivars low in polyphenolics with cultivars rich in polyphenolics, consuming apples grown in particular regions known to induce higher concentrations of polyphenolics, and because about half of the apple polyphenols are present in the skin, ensuring that the skin is consumed during fresh consumption or is included in processed apple products. These measures could potentially double the consumption of apple polyphenolics resulting in improvements in health and well-being.

ACKNOWLEDGMENT

Sue Davies, Ross Marshall, Kylie Miller, Iain Latter collected apple samples at the HortResearch stations in Clyde, Nelson, and Hawke's Bay. Patrick Connolly provided assistance with the statistical analysis.

LITERATURE CITED

(1) Block, G.; Patterson, B.; Subar, A. Fruit, vegetables, and cancer prevention: A review of the epidemiological evidence. *Nutr. Cancer* **1992**, *18*, 1−29.

(2) Steinmetz, K. A.; Potter, J. D. Vegetables, fruit, and cancer prevention: A review. *J. Am. Diet. Assoc.* **1996**, *96*, 1027−1039.

(3) Joshipura, K. J.; Hu, F. B.; Manson, J. E.; Stampfer, M. J.; Rimm, E. B.; Speizer, F. E.; Colditz, G.; Ascherio, A.; Rosner, B.; Spiegelman, D.; Willett, W. C. The effect of fruit and vegetable intake on risk for coronary heart disease. *Ann. Intern. Med.* **2001**, *134*, 1106−1114.

(4) Riboli, E.; Norat, T. Epidemiologic evidence of the protective effect of fruit and vegetables on cancer risk. *Am. J. Clin. Nutr.* **2003**, *78* (supplement), 559S−569S.

(5) Anon. Diet, nutrition, and the prevention of chronic diseases. World Health Organisation, 2003.

(6) Ames, B. N.; Shigenaga, M. K.; Hagen, T. M. Oxidants, antioxidants, and the degenerative diseases of aging. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 7915−7922.

(7) Knekt, P.; Kumpulainen, J.; Jarvinen, R.; Rissanen, H.; Heliovaara, M.; Reunanen, A.; Hakulinen, T.; Aromaa, A. Flavonoid intake and risk of chronic diseases. *Am. J. Clin. Nutr.* **2002**, *76*, 560−568.

(8) Hertog, M. G. L.; Feskens, E. J. M.; Hollman, P. C. H.; Katan, M. B.; Kromhout, D. Dietary antioxidant flavonoids and risk of coronary heart disease: The Zutphen Elderly Study. *Lancet* **1993**, *342*, 1007−1011.

(9) Vinson, J. A.; Su, X.; Zubik, L.; Bose, P. Phenol antioxidant quantity and quality in foods: Fruit. *J. Agric. Food Chem.* **2001**, *49*, 5315−5321.

(10) Hertog, M. G. L.; Hollman, P. C. H.; Katan, M. B.; Kromhout, D. Intake of potentially anticarcinogenic flavonoids and their determinants in adults in The Netherlands. *Nutr. Cancer* **1993**, *20*, 21−29.

(11) Sampson, L.; Rimm, E. B.; Hollman, P. C. H.; De Vries, J. H. M.; Katan, M. B. Flavonol and flavone intakes in US health professionals. *J. Am. Diet. Assoc.* **2002**, *102*, 1414−1420.

(12) Lee, K. W.; Kim, Y. J.; Kim, D.-O.; Lee, H. J.; Lee, C. Y. Major phenolic in apple and their contribution to the total antioxidant capacity. *J. Agric. Food Chem.* **2003**, *51*, 6516−6520.

(13) Chinnici, F.; Bendini, A.; Gaiani, A.; Riponi, C. Radical scavenging activities of peels and pulps from cv. Golden Delicious apples as related to their phenolic composition. *J. Agric. Food Chem.* **2004**, *52*, 4684−4689.

(14) Lu, Y.; Foo, L. Y. Antioxidant and radical scavenging activities of polyphenols from apple pomace. *Food Chem.* **2000**, *68*, 81−85.

(15) Oleszek, W.; Lee, C. Y.; Jaworski, A. W.; Price, K. R. Identification of some phenolic compounds in apples. *J. Agric. Food Chem.* **1988**, *36*, 430−432.

(16) Lu, Y.; Foo, L. Y. Identification and quantification of major polyphenols in apple pomace. *Food Chem.* **1997**, *59*, 187−194.

(17) Tsao, R.; Yang, R.; Young, J. C.; Zhu, H. Polyphenolic profiles in eight apple cultivars using high-performance liquid chromatography (HPLC). *J. Agric. Food Chem.* **2003**, *51*, 6347−6353.

(18) van der Sluis, A. A.; Dekker, M.; de Jager, A.; Jongen, W. M. F. Activity and concentration of polyphenolic antioxidants in apple: Effect of cultivar, harvest, and storage conditions. *J. Agric. Food Chem.* **2001**, *49*, 3606−3613.

(19) Escarpa, A.; Gonzalez, M. C. High-performance liquid chromatography with diode-array detection for the determination of phenolic compounds in peel and pulp from different apple varieties. *J. Chromatogr., A* **1998**, *823*, 331−337.

(20) Awad, M. A.; de Jager, A. Relationships between fruit nutrients and concentratioins of flavonoids and chlorogenic acids in Elstar apple skin. *Sci. Hortic.* **2002**, *92*, 265−276.

(21) Awad, M. A.; de Jager, A.; van Westing, L. M. Flavonoid and cholorgenic acid levels in apple fruit: Characterisation of variation. *Sci. Hortic.* **2000**, *83*, 249−263.

(22) Lister, C. E.; Lancaster, J. E.; Sutton, K. H.; Walker, J. R. L. Developmental changes in the concentration and composition of flavonoids in skin of a red and a green apple cultivar. *J. Sci. Food Agric.* **1994**, *64*, 155−161.

(23) Reay, P. F. The role of low temperatures in the development of the red blush on apple fruit ("Granny Smith"). *Sci. Hortic.* **1999**, *79*, 113−119.

(24) Rice-Evans, C. A.; Miller, N. J.; Paganga, G. Structure−antioxidant activity relationships of flavonoids and phenolic acids. *Free Radical Biol. Med.* **1996**, *20*, 933−956.

(25) Cao, G.; Sofic, E.; Prior, R. L. Antioxidant and prooxidant behaviour of flavonoids: Structure−activity relationships. *Free Radical Biol. Med.* **1997**, *22*, 749−760.

(26) Prior, R. L.; Cao, G.; Martin, A.; Sofic, E.; McEwen, J.; O'Brien, C.; Lischner, N.; Ehlenfeldt, M.; Kalt, W.; Krewer, G.; Mainland, C. M. Antioxidant capacity as influenced by total phenolic and anthocyanin content, maturity, and variety of Vaccinium species. *J. Agric. Food Chem.* **1998**, *46*, 2686−2693.

Received for review December 22, 2004. Accepted February 7, 2005. The study was funded by the New Zealand Foundation for Research Science and Technology Contract C06X0005.

JF047832R