Food Chemistry 116 (2009) 202–207

Contents lists available at ScienceDirect

Food Chemistry

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

A survey of Irish fruit and vegetable waste and by-products as a source of polyphenolic antioxidants

Hilde H. Wijngaard *, Christian Rößle, Nigel Brunton

Teagasc Ashtown Food Research Centre, Ashtown, Dublin 15, Ireland

ARTICLE INFO

Article history:
Received 25 November 2008
Received in revised form 9 January 2009
Accepted 16 February 2009

Keywords:
Fruits waste
Vegetable by-products
Antioxidant activity
Polyphenols
HPLC–DAD
FRAP
DPPH
Folin–Ciocalteu

ABSTRACT

In this study, fruit and vegetable by-product and waste sources in Ireland were tested for their antioxidant activity and polyphenol content. The highest levels of antioxidants measured by both ferric reducing antioxidant power (FRAP) and diphenyl-picrylhydrazyl (DPPH) assays, were detected in whole kiwifruit. Of the vegetable by-products, broccoli stems showed the best antioxidant potential. The level of polyphenols as assessed by the Folin–Ciocalteu Reagent (FCR) was significantly correlated with the level of polyphenols by HPLC–DAD ($r = 0.93$). The level of polyphenols assessed by HPLC–DAD was not significantly correlated with the antioxidant assays. Apple pomace and vegetable by-products were found to be good sources of both polyphenols and antioxidants and due to their abundance may be exploitable resources to use as food ingredients.

1. Introduction

Fruits and vegetable processing in Ireland generates substantial quantities of waste/by-products (Environmental Protection Agency, 2003). It has been previously reported that waste and by-products of fruits may be an abundant source of antioxidant polyphenols (Balasundram, Sundram, & Samman, 2006; Peschel et al., 2006). At the present time, fruit and vegetable waste and by-products are disposed of often at a cost to the manufacturer. Therefore, use of the waste as a source of polyphenols may be of considerable economic benefit to food processors. Fruit and vegetable waste and by-products can range from pomace (leftovers after pressing), to cabbage cut-offs and whole fruits and vegetables.

Polyphenols are common constituents of the human diet, with fruits and vegetables being the major dietary source of these bioactive compounds. The possible health benefits of polyphenol consumption have been suggested to derive from their antioxidant and anti-inflammatory properties (Joseph, Shukitt-Hale, & Casadesus, 2005; Mertens-Talcott, Jilma-Stohlawetz, Rios, Hingorani, & Derendorf, 2006). Evidence for their role in the prevention of degenerative diseases is emerging. Experimental studies on animals and human cell lines have demonstrated that polyphenols can play a role in the prevention of cancer and cardiovascular diseases (Scalbert, Manach, Morand, Rémésy, & Jiménez, 2005).

In this study potential of fruit and vegetable waste and by-products obtained from the Irish fruit and vegetable industry as a source of antioxidant compounds was examined. Ingredients with high polyphenol content could be developed from fruit and vegetable waste streams to act as healthy components in foods. In addition to their potential health benefit, natural extracts high in antioxidant activity can be added to food products to preserve their colour and flavour and hence improve their shelflife (Moure et al., 2001). In this study, by-product and waste sources in Ireland were selected, and their antioxidant activity and polyphenol content was assessed. Methanolic extracts were tested, since preliminary studies showed that methanolic extraction contained the highest antioxidant potential. In later studies, extraction of the potent antioxidants with food safe solvents and methods will be optimised.

2. Materials and methods

2.1. Chemicals

Kuromanin, apigenin, vitexin, luteolin, cyanidin, and naringenin were purchased from Extrasynthèse (Lyon, France). Chlorogenic acid, ferulic acid, trans-4-hydroxy-3-methoxy cinnamic acid, caffeic acid, gallic acid, ellagic acid, quercetin, rutin, myricetin, narin-

* Corresponding author. Tel.: +353 (0)1 805 9500; fax: +353 (0)1 805 9550.
E-mail addresses: Hilde.wijngaard@teagasc.ie (H.H. Wijngaard), Christian.roessle@teagasc.ie (C. Rößle), Nigel.brunton@teagasc.ie (N. Brunton).

0308-8146/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2009.02.033

gin, phloridzin, epicatechin, kaempferol and 2,2-diphenyl-1-picrylhydrazyl (DPPH), 2,4,6-tris(2-pyridyl)-s-triazine (TPTZ), 6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (Trolox) and Folin–Ciocalteu Reagent (FCR) were purchased from Sigma–Aldrich Chemical Co. (St. Louis, USA).

2.2. Preparation of materials

Cauliflower cut-offs (cv. Cornell), white cabbage cut-offs (cv. Cilion) and broccoli stems (cv. Monaco) were provided by Nature's Best (Drogheda, Ireland), and apple pomace was provided by Bulmers limited (Clonmel, Ireland). Fruit and vegetable waste samples (kiwifruits (cv. Hayward), pink grapefruits (cv. Red Star Ruby), apples (cv. Pink Lady), and lettuce (cv. Iceberg)) were provided by an Irish distributing company of fruits and vegetables (Keelings Fruit Importers, St. Margaret's, Ireland). Kiwifruits and grapefruits were divided in whole, peel, and flesh samples; the apples were divided in whole, peel, flesh, and core (including seeds) samples and lettuces were divided in whole, outer leaves and core samples. Where applicable, samples were cut in slices of less than 10 mm, vacuum packed and stored at −20 °C for at least 24 h. Following this, samples were removed from the vacuum pack and lyophilised for a minimum of 5 days in an A6/14 freeze dryer (Frozen in Time Ltd., York, UK). The lyophilised samples were then vacuum packed and stored at −20 °C until required for analysis.

2.3. Extraction of antioxidants

Each sample was extracted in triplicate. On the day of extraction, samples were milled to a fine powder using a blender (BL440001, Kenwood limited, Hampshire, UK). After adding 25 ml of methanol to 1.25 g sample powder, the samples were homogenised for 70 s at 24,000 rpm using an Ultra – Turrax T-25 tissue homogeniser (IKA-group, Saufen, Germany). The samples were vortexed with a V400 Multituve Vortexer (Alpha laboratories, North York, Canada) for 20 min at 1050 rpm and centrifuged for 10 min at 2000 rpm (MSE Mistral 3000i, Sanyo Gallenkamp, Leicestershire, UK). Ten millilitres of the supernatant was filtered through 0.22 μm PTFE syringe filters (Phenomenex, Macclesfield Cheshire, UK). The extracts were stored at −20 °C.

2.4. Antioxidant activity methods

As recommended by Stratil, Klejdus, and Kuban (2006), Trolox was used as a standard in the ferric reducing antioxidant power (FRAP) and DPPH assays. Standard samples were prepared by diluting a methanolic Trolox stock solution (0.2 mM). The Trolox standard samples and blanks were used to make a calibration curve. The results are expressed in milligrams Trolox equivalent/100 g dry weight (mg TE 100 g^{-1} DW).

2.5. DPPH assay

A modified version of the DPPH method (Goupy, Hugues, Boivin, & Amiot, 1999) was used. A working DPPH solution (0.048 mg ml^{-1}) was prepared by making a 1 in 5 dilution of the methanolic DPPH stock solution (2.38 mg ml^{-1}). Prior to analysis, serial dilutions of the methanolic extracts of the fruit samples were prepared. Diluted sample (500 μl) and DPPH working solution (500 μl) were added to a micro-centrifuge tube. After vortexing, the tubes were left in the dark for 30 min at room temperature. The absorbance was then measured against methanol at 515 nm in 1 ml cuvettes using a spectrophotometer (UV-1700 Pharma Spec, Shimadzu, Milton Keynes). The decrease in absorbance of a sample was calculated in comparison to a blank sample (500 μl methanol and 500 μl DPPH). The relative decrease in absorbance (PI) was then calculated as follows: PI (%) = $1 - (A_e/A_b)$, with A_e = absorbance of sample extract and A_b = absorbance of blank. The PIs used to calculate the related antioxidant activity were superior (PI_1) and inferior (PI_2) to the value estimated at 50%. The antioxidant activity was defined as the concentration of sample extract necessary to obtain an activity of 50% (IC_{50}). In all experiments the IC_{50} of Trolox was determined as well. The final results for antioxidant activity were determined by using the following equation: antioxidant activity = $(IC_{50Trolox}/IC_{50Sample}) \times 10^5$ (Hagen et al., 2007). The antioxidant activity was expressed in mg Trolox equivalent (TE) per 100 g dry weight sample (mg TE 100 g^{-1} DW), to facilitate comparison with results from ferric reducing antioxidant power (FRAP) assay.

2.6. FRAP assay

The FRAP assay was carried out according to Stratil et al. (2006) with slight modifications. The FRAP solution was freshly prepared on the day of use, by mixing acetate buffer (pH 3.6), ferric chloride solution (20 mM) and TPTZ solution (10 mM TPTZ in 40 mM HCl) in a proportion of 10:1:1, respectively. Following this the FRAP solution was heated, while protected from light, until it had reached a temperature of 37 °C. Appropriate dilutions of methanolic fruit extracts were prepared. One hundred microlitres of the diluted sample extract (or for blank 100 μl methanol and for Trolox standard curves 100 μl Trolox of appropriate concentration) and 900 μl of FRAP solution were added into a micro-centrifuge tubes. The tubes were vortexed and left at 37 °C for exactly 40 min, and the absorbance was measured at 593 nm. The Trolox standard curves were used to calculate the antioxidant activity of the samples in relation to Trolox and were expressed as mg Trolox equivalent/100 g dry weight sample (mg TE 100 g^{-1} DW).

2.7. Polyphenol analysis

2.7.1. FCR assay

Total phenolic content of methanolic fruit extracts was assessed using a modified version of the Folin–Ciocalteu assay (Singelton, Orthofer, & Lamuela-Raventos, 1999). Gallic acid was used as a standard and the aqueous gallic acid solution (200 mg l^{-1}) was diluted with distilled water to give appropriate concentrations for a standard curve. For the analysis, 100 μl of methanolic fruit extract or gallic acid standard, 100 μl of methanol, 100 μl of Folin–Ciocalteu reagent and 700 μl of Na_2CO_3 were added into 1.5 ml micro-centrifuge tube. The samples were vortexed immediately and the tubes were incubated in the dark for 20 min at room temperature. After incubation all samples were centrifuged at 13,000 rpm for 3 min. The absorbance of the supernatant was then measured at 735 nm in 1 ml plastic cuvettes using a spectrophotometer (UV-1700 Pharma Spec, Shimadzu, Japan). The results were expressed in mg gallic acid equivalent/100 g dry weight (mg GAE 100 g^{-1} DW).

2.7.2. HPLC-DAD

HPLC-analysis was performed on a Varian Pro Star (Varian Inc., Walnut Creek, USA) chromatography system, equipped with a module 210 solvent delivery system, a module 510 column thermostat, a module 410 autosampler and a module 335 diode array detector (DAD) with an absorbance detection range between 190 and 950 nm. Separations were conducted on a Zorbax SB C_{18}, 5 μm, 150 × 4.6 mm column (Agilent Technologies, Dublin, Ireland). The gradient profile was based on a method of Tsao and Yang (2003). Acetic acid in 2 mM sodium acetate (final pH 2.55, v/v) was used as eluent A and 100% acetonitrile was used as eluent B. The column temperature was set at 37 °C and the flow rate was 1 ml min^{-1}. The solvent gradient programme was set as follows:

initial conditions 100% A, 0% B; 0–45 min, 0–15% B; 45–60 min, 15–30% B; 60–65 min, 30–50% B; 65–70 min, 50–100% B. Prior to injection sample extracts were filtered with PTFE syringe 0.22 μm filters. The injection volume was 10 μl. Hydroxybenzoic acids, dihydrochalcones, flavanones and flavanols were monitored at a wavelength of 280 nm, hydroxycinnamic acid derivatives at 320 nm, flavonols at 360 nm and anthocyanins at 520 nm. For quantification and identification purposes standard curves of analytes of interest were prepared using methanolic solutions of the standards listed above.

2.8. Statistics

All samples were prepared and analysed in triplicate. Data are presented in means ± their standard deviation. The Pearson correlation coefficient (r) and propability-value (p) were used to show correlation and their significance by using Minitab (MINITAB 15.1.1.0, 2007). A probability value of $p < 0.05$ was considered statistically significant. For correlations, which included HPLC results, only fruit samples were considered.

3. Results and discussion

3.1. Antioxidant activity (DPPH and FRAP) and polyphenol content (FCR)

Table 1 shows the antioxidant activity of all samples assessed using the FRAP and DPPH assays. The antioxidant assays FRAP and DPPH were very well correlated (Table 2), with a significant correlation coefficient of $r = 0.95$, which agrees with results from other authors (Stratil et al., 2006; Thaipong, Boonprakob, Crosby, Cisneros-Zevallos, & Hawkins Byrne, 2006).

Whole kiwifruits had highest antioxidant activity of all samples (Table 1). Methanolic extracts from kiwifruit also had the highest antioxidant activity in both flesh and peel (Table 3). In contrast, apple extracts exhibited moderate antioxidant activity in the flesh as measured by DPPH and FRAP, which was reflected in a lower antioxidant activity for the whole apple. In general, outer parts of fruit and vegetables contained more antioxidants as compared to the flesh (Table 3). The exception was the outer leaves of the Iceberg lettuce, which had lower antioxidant activity in the outer leaves as measured using the DPPH and FRAP assays. The concentration of antioxidants is often higher in the outer regions of the plant or fruit, since antioxidants play a protective role in plants (Manach, Scalbert, Morand, Remesy & Jimenez, 2004).

Amongst the vegetable waste and by-products, broccoli stems contained the highest antioxidant activity, while whole iceberg lettuce had the lowest activity in both assays. Surprisingly iceberg lettuce cores had similar levels of polyphenols and antioxidants to cabbage and cauliflower cut-offs.

As is shown in Table 2, the polyphenol content as measured by FCR, correlated significantly with the antioxidant activity values from the FRAP and DPPH assays ($r = 0.72$ for both correlations). In addition to the fact that polyphenol levels may be related to antioxidant activity, the FCR method is in principal also a reduction/oxidation method. As a result the FCR assay also measures some non-polyphenolic compounds such as carotenoids and ascorbic acid (George, Brat, Alter, & Amiot, 2005; Huang, Ou, & Prior, 2005). Broccoli from the vegetable samples and whole grapefruit from the fruit samples had the highest total polyphenol composition as assessed using the FCR assay. As can be seen in Table 3, both the flesh and the peel of the red grapefruit were high in polyphenols as assessed by FCR. Another good resource of phenols as measured by FCR was apple pomace (870 mg GAE 100 g^{-1}). Apple core had a higher phenol content than the apple flesh, which is most likely due to the fact that the seeds contained within the core, are higher in phenolics than the flesh (Schieber et al., 2003). Apple peel is also high in polyphenols and antioxidants (Table 3). Therefore, apple pomace, which consists primarily of peels and cores of pressed apples, was found to be a useful resource for polyphenols and antioxidants (Table 1). This is in agreement with Peschel et al. (2006), who also reported that apple pomace was a promising source of antioxidant components.

Table 2
Correlation matrix showing relationship between antioxidant indices (FRAP and DPPH), total phenols (FCR) and HPLC measurement of phenolic compounds for methanolic extracts from fruit and vegetable by-products.

	DPPH	FRAP	FCR	HPLC
DPPH	1			
FRAP	0.954*	1		
FCR	0.724*	0.721*	1	
HPLC**	Not significant	Not significant	0.934*	1

* Correlation is significant with p-value < 0.001.
** Only results from fruit waste by-products were used, since not all polyphenols in vegetable samples could be identified.

3.2. Polyphenols by HPLC-DAD

The presence of seven different polyphenol groups was detected by HPLC-DAD in the fruit samples by comparison of their UV–Vis spectra with spectra of standard compounds and reported values (Table 4). The sum of the individual levels of the polyphenol groups was used to calculate the total polyphenol content of the extracts. Using this method, whole grapefruit had the highest amount of polyphenols (12,689 ± 111 μmol 100 g^{-1} DW), while the whole kiwifruit contained very low levels of polyphenols (17.7 ± 1.5 μmol 100 g^{-1} DW). A good significant correlation of $r = 0.93$ (Table 2) was found between the levels of total polyphenols as assessed using the FCR assay and sum of the individual polyphenols as monitored by HPLC-DAD. Therefore the FCR assay could be used as a quick screening method for total phenol level. If there is interest in specific pol-

Table 1
Antioxidant activity as determined by FRAP and DPPH assays and total phenol content measured by FCR of methanolic extracts from freeze-dried fruit and vegetable waste and by-products. Mean values and standard deviations are presented.

Freeze-dried material		FRAP (mg TE 100 g^{-1} DW)[a]	DPPH (mg TE 100 g^{-1} DW)	FCR (mg GAE 100 g^{-1} DW)[b]
Whole fruit and vegetable waste	Apple cv. Pink Lady	949 ± 26	383 ± 9	636 ± 60
	Kiwifruit cv. Hayward	1709 ± 16	762 ± 15	752 ± 16
	Pink Grapefruit cv. Red Star Ruby	1477 ± 20	700 ± 18	1867 ± 31
	Lettuce cv. Iceberg	196 ± 1	67 ± 3	164 ± 4
By-product	Apple pomace	1435 ± 34	636 ± 25	870 ± 13
	White cabbage cut-offs	449 ± 9	284 ± 10	341 ± 6
	Cauliflower cut-offs	535 ± 12	200 ± 14	402 ± 11
	Broccoli stems	761 ± 9	512 ± 24	494 ± 6

[a] mg Trolox equivalent/100 g dry weight sample.
[b] mg gallic acid equivalent/100 g dry weight sample.

Table 3
Antioxidant activity as determined by FRAP and DPPH assays and total phenol content measured by FCR of fruit methanolic extracts. Mean values and standard deviations are presented.

Raw material	Part	FRAP (mg TE 100 g^{-1} DW)[a]	DPPH (mg TE 100 g^{-1} DW)	FCR (mg GAE 100 g^{-1} DW)[b]
Apple cv. Pink Lady	Peel	1701 ± 29	919 ± 7	1144 ± 14
	Flesh	721 ± 5	273 ± 6	467 ± 5
	Core	1422 ± 40	668 ± 43	836 ± 5
Kiwifruit cv. Hayward	Peel	1803 ± 33	919 ± 31	820 ± 25
	Flesh	1620 ± 12	735 ± 14	550 ± 17
Pink Grapefruit cv. Red Star Ruby	Peel	1389 ± 32	633 ± 20	2335 ± 97
	Flesh	1210 ± 25	516 ± 21	2095 ± 45
Lettuce cv. Iceberg	Outer Leaves	339 ± 25	79 ± 2	189 ± 13
	Core	429 ± 30	168 ± 8	257 ± 23

[a] mg Trolox equivalent/100 g dry weight sample.
[b] mg gallic acid equivalent/100 g dry weight sample.

Table 4
Levels (μmol 100 g^{-1} DW) of polyphenol groups present in range of fruit samples.

Sample	Cultivar	Polyphenol group	μmol 100 g^{-1} DW
Apple pomace		Flavonolglycosides[a]	120 ± 5.7
		Hydroxy cinnamic acids[b]	79 ± 2.6
		Dihydrochalcones[c]	126 ± 8.9
		Total	*324 ± 9.5*
Whole apple	Pink Lady	Flavonolglycosides	21 ± 0.7
		Flavanols[d]	283 ± 24
		Hydroxy cinnamic acids	349 ± 2.5
		Dihydrochalcones[d]	88 ± 27
		Anthocyanins[e]	23 ± 0.4
		Total	*764 ± 17*
Peel apple	Pink Lady	Flavonolglycosides	537 ± 21
		Flavanols	1487 ± 17
		Hydroxy cinnamic acids	209 ± 4.2
		Dihydrochalcones	84 ± 13
		Anthocyanins	74 ± 1.7
		Total	*2390 ± 39*
Core apple	Pink Lady	Flavonolglycosides	19 ± 0.5
		Hydroxy cinnamic acids	682 ± 28
		Dihydrochalcones	577 ± 64
		Total	*1278 ± 92*
Flesh apple	Pink Lady	Hydroxy cinnamic acids	297 ± 7.8
		Total	*297 ± 7.8*
Whole kiwifruit	Hayward	Hydroxy cinnamic acids	17.7 ± 1.5
		Total	*17.7 ± 1.5*
Peel kiwifruit	Hayward	Flavonolglycosides	311 ± 13
		Flavanols	327 ± 4.0
		Hydroxy cinnamic acids	290 ± 12
		Total	*928 ± 15*
Flesh kiwifruit	Hayward	Hydroxy cinnamic acids	28 ± 2.3
		Total	*28 ± 2.3*
Whole grapefruit	Red Star Ruby	Hydroxy cinnamic acids	955 ± 33
		Flavanones[f]	11,631 ± 138
		Flavones[g]	103 ± 10
		Total	*12,689 ± 111*
Peel grapefruit	Red Star Ruby	Hydroxy cinnamic acids	1972 ± 8.6
		Flavanones	20,192 ± 1436
		Flavones	139 ± 18
		Total	*22,303 ± 1443*
Flesh grapefruit	Red Star Ruby	Hydroxy cinnamic acids	418 ± 51
		Flavanones	9990 ± 868
		Flavones	40 ± 2.8
		Total	*10,448 ± 898*

Levels expressed in mg 100 g^{-1} DW: (a) rutin (λ_{max} = 256/354 nm); (b) chlorogenic acid (λ_{max} = 239/295shoulder/325 nm); (c) phloridzin (λ_{max} = 285 nm); (d) epicatechin (λ_{max} = 237/277 nm); (e) cyanidin (λ_{max} = 245shoulder/274/440shoulder/520 nm); (f) naringin (λ_{max} = 283 /330shoulder nm) and (g) vitexin (λ_{max} = 268/336 nm).

yphenol composition the HPLC-DAD method should be applied. However for some samples total polyphenol level as monitored by HPLC-DAD was not well correlated with FCR measurements. Whole kiwifruit, for example, was high in polyphenols as measured by FCR (752 mg GAE 100 g^{-1} DW) but contained very little polyphenols when quantified by HPLC-DAD (17.7 ± 1.5 μmol 100 g^{-1} DW). Kiwifruits are good sources of ascorbic acid with up to 10 times higher levels than apples and pears (Szeto, Tomlinson, & Benzie, 2002). Therefore, high levels of ascorbic acid present in kiwifruit flesh may have resulted in an overestimation of polyphenols in

kiwifruit flesh by FCR (George et al., 2005). High levels of non-polyphenolic antioxidants, such as ascorbic acid, also explains why whole kiwifruit had the highest antioxidant potential in the DPPH and FRAP assays, but the lowest polyphenol level by HPLC-DAD.

There was no significant correlation found between either the DPPH or FRAP assay and the total level of polyphenols detected by HPLC-DAD. This can be explained by the fact that the individual polyphenols present in fruit and vegetable samples have different relative antioxidant potencies. For instance, aglycones show a higher antioxidant activity than their related glycosides. Another example is the flavanone naringin present in grapefruit, which has a relatively low antioxidant activity as measured by DPPH (Bandoniene, Murkovic, Pfannhauser, Venskutonis, & Gruzdiene, 2002). In addition, non-polyphenolic compounds like ascorbic acid, will not be measured by the HPLC-DAD method, but will contribute to antioxidant activity. For example, in addition to polyphenols broccoli and red grapefruit contain significant levels of vitamin C (Singh, Upadhyay, Prasad, Bahadur, & Rai, 2007; Vanamala et al., 2005).

Some polyphenol groups in the vegetable by-product samples could not be identified and hence no total estimation of polyphenols by HPLC could be established.

3.3. Polyphenol composition

HPLC-DAD was used to identify polyphenol groups based on their UV–Vis wavelength spectrum and retention time. In the fruit samples flavonols, dihydrochalcones, hydroxycinnamic acids, anthocyanins, flavanols, flavones and flavanones (Table 4) were present. As outlined by Tsao and Yang (2003), total levels of polyphenols were expressed as equivalents of the most abundant representative of the polyphenol group present where possible (Table 4). Anthocyanins were only detected in apple peel and therefore the whole apple. In fact, one anthocyanin, cyanidin-3-glucoside or kuromanin, was present in apple peel. Other authors have also reported the presence of kuromanin in Pink Lady apple skin (Whale & Zora, 2007). As recommended by Koponen, Happonen, Mattila & Torronen (2007) the aglycone cyanidin was used to quantify the anthocyanin level. Grapefruit samples were the only samples, which contained flavones. Sakakibara, Honda, Nakagawa, Ashida, and Kanazawa (2003) also identified apigenin glucosides in grapefruits and Mullen, Marks, and Crozier (2007) have reported apigenin glucosides in grapefruit juice. Hydroxycinnamic acids were detected in all fruit samples, but there was qualitative differences in the cinnamic acids identified (Lu & Yeap Foo, 1998). In kiwifruit, cinnamic acids were the only polyphenols detected and caffeic acid was the major cinnamic acid present. Other authors also reported caffeic acid to be the most prominent phenolic acid in kiwifruit. However, other phenolic acids, such as protocatechuic acid and *p*-coumaric acid, have also been detected (Mattila, Hellstrom & Torronen, 2006). The only hydroxy cinnamic acid detected in apple was chlorogenic acid, while grapefruit contained a range of cinnamic acids. In general, grapefruit samples had a different polyphenol composition in comparison to kiwifruit waste and apple pomace and apple waste (Table 4). In addition to flavones, grapefruit samples contained flavanones. Naringin, a naringenin glucoside contributed up to approximately 92% of the total polyphenol level of the whole grapefruit. Besides flavanones, whole pink grapefruit samples had high levels of cinnamic acids, which is in agreement with other reports (Gorinstein et al., 2001).

In apple samples, the highest polyphenol level was detected in the peel, followed by the core which contained approximately half the amount of polyphenols of the peel. The flesh only contained chlorogenic acid. Apple pomace, a by-product from the pressing of apples of different varieties was found to have higher levels of polyphenols than the Pink Lady apple flesh. Apple pomace mainly consists of cores and peels.

Vegetable samples were abundant in hydroxy cinnamic acid, cinnamic acid conjugates and polyphenol groups with maxima at approximately 275 nm. In white cabbage and cauliflower cinnamic acid conjugates with identical retention times were detected. They eluted much later than simple cinnamic acids, but have a similar wavelength spectrum. These polyphenols could not be identified, but are probably highly glycosylated flavonoids, as described in literature (Llorach, Gil-Izquierdo, Ferreres & Tomas-Barberan, 2003).

4. Conclusions

Whole fruit waste could serve as a potent source of polyphenols and antioxidants, but due to the range of varieties used and the relatively low level generated, it is probably not a good resource for the functional ingredient industry. Apple pomace on the other hand is high in antioxidants and polyphenols, food grade and present in abundance. Vegetable by-products also have good potential as sources of polyphenols and more research should be carried out to identify other possible antioxidants and bioactive compounds in these resources. This would also entail an optimisation of their extraction. A high polyphenol level does not always imply a high antioxidant level. This should be taken in consideration when designing an industrial ingredient. Fruit waste and by-products generally show a higher antioxidant activity than vegetable waste and by-products.

List of common abbreviations

DPPH	2,2-diphenyl-1-picrylhydrazyl
FRAP	ferric reducing antioxidant power
TPTZ	2,4,6-tris(2-pyridyl)-s-triazine
FCR	Folin–Ciocalteu Reagent
Trolox	6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid
PI	relative decrease in absorbance
IC_{50}	concentration of sample extract necessary to obtain an activity of 50%
TE	trolox equivalent
DW	dry weight
GAE	gallic acid equivalent
DAD	diode array detector
p	probability value
r	Pearson correlation coefficient

Acknowledgements

The authors would like to thank Keelings Fruit Importers, Nature's Best, and Bulmers Limited for supplying the samples. We would also like to acknowledge the Food Institutional Research Measure (FIRM) 2006 program from the Irish Department of Agriculture and Food for the funding of this research.

References

Balasundram, N., Sundram, K., & Samman, S. (2006). Phenolic compounds in plants and agri-industrial by-products: Antioxidant activity, occurrence, and potential uses. *Food Chemistry, 99*(1), 191–203.

Bandoniene, D., Murkovic, M., Pfannhauser, W., Venskutonis, P. R., & Gruzdiene, D. (2002). Detection and activity evaluation of radical scavenging compounds by using DPPH free radical and on-line HPLC-DPPH methods. *European Food Research and Technology, 214*(2), 143–147.

Environmental Protection Agency (2003). The National waste database. *Interim Report* (p. 32): Environmental Protection Agency.

George, S., Brat, P., Alter, P., & Amiot, M. J. (2005). Rapid determination of polyphenols and vitamin C in plant-derived products. *Journal of Agricultural and Food Chemistry, 53*(5), 1370–1373.

Gorinstein, S., Martin-Belloso, O., Park, Y.-S., Haruenkit, R., Lojek, A., Ciz, M., et al. (2001). Comparison of some biochemical characteristics of different citrus fruits. *Food Chemistry, 74*(3), 309–315.

Goupy, P., Hugues, M., Boivin, P., & Amiot, M. J. (1999). Antioxidant composition and activity of barley (Hordeum vulgare) and malt extracts and of isolated phenolic compounds. *Journal of the Science of Food and Agriculture, 79*(12), 1625–1634.

Hagen, S. F., Borge, G. I. A., Bengtsson, G. B., Bilger, W., Berge, A., Haffner, K., et al. (2007). Phenolic contents and other health and sensory related properties of apple fruit (Malus domestica Borkh., cv. Aroma): Effect of postharvest UV-B irradiation. *Postharvest Biology and Technology, 45*(1), 1–10.

Huang, D., Ou, B., & Prior, R. L. (2005). The chemistry behind antioxidant capacity assays. *Journal of Agricultural and Food Chemistry, 53*(6), 1841–1856.

Joseph, J. A., Shukitt-Hale, B., & Casadesus, G. (2005). Reversing the deleterious effects of aging on neuronal communication and behavior: Beneficial properties of fruit polyphenolic compounds. *American Journal of Clinical Nutrition, 81*, 313S–316S.

Koponen, J. M., Happonen, A. M., Mattila, P. H., & Torronen, A. R. (2007). Contents of anthocyanins and ellagitannins in selected foods consumed in finland. *Journal of Agricultural and Food Chemistry, 55*(4), 1612–1619.

Llorach, R., Gil-Izquierdo, A., Ferreres, F., & Tomas-Barberan, F. A. (2003). HPLC-DAD-MS/MS ESI characterization of unusual highly glycosylated acylated flavonoids from cauliflower (*Brassica oleracea L. var. botrytis*) agroindustrial byproducts. *Journal of Agricultural and Food Chemistry, 51*(13), 3895–3899.

Lu, Y., & Yeap Foo, L. (1998). Constitution of some chemical components of apple seed. *Food Chemistry, 61*(1-2), 29–33.

Manach, C., Scalbert, A., Morand, C., Remesy, C., & Jimenez, L. (2004). Polyphenols: Food sources and bioavailability. *American Journal of Clinical Nutrition, 79*(5), 727–747.

Mattila, P., Hellstrom, J., & Torronen, R. (2006). Phenolic acids in berries, fruits, and beverages. *Journal of Agricultural and Food Chemistry, 54*(19), 7193–7199.

Mertens-Talcott, S. U., Jilma-Stohlawetz, P., Rios, J., Hingorani, L., & Derendorf, H. (2006). Absorption, metabolism, and antioxidant effects of pomegranate (*Punica granatum* L.) polyphenols after ingestion of a standardized extract in healthy human volunteers. *Journal of Agricultural and Food Chemistry, 54*(23), 8956–8961.

Moure, A., Cruz, J. M., Franco, D., Domínguez, J. M., Sineiro, J., Domínguez, H., et al. (2001). Natural antioxidants from residual sources. *Food Chemistry, 72*, 145–171.

Mullen, W., Marks, S. C., & Crozier, A. (2007). Evaluation of phenolic compounds in commercial fruit juices and fruit drinks. *Journal of Agricultural and Food Chemistry, 55*(8), 3148–3157.

Peschel, W., Sanchez, R. F., Diekmann, W., Plescher, A., Gartzia, I., Jimenez, D., et al. (2006). An industrial approach in the search of natural antioxidants from vegetable and fruit wastes. *Food Chemistry, 97*(1), 137–150.

Sakakibara, H., Honda, Y., Nakagawa, S., Ashida, H., & Kanazawa, K. (2003). Simultaneous determination of all polyphenols in vegetables, fruits, and teas. *Journal of Agricultural and Food Chemistry, 51*(3), 571–581.

Scalbert, A., Manach, C., Morand, C., Rémésy, C., & Jiménez, L. (2005). Dietary polyphenols and the prevention of diseases. *Critical Reviews in Food Science and Nutrition, 45*(4), 287–306.

Schieber, A., Hilt, P., Streker, P., Endress, H. U., Rentschler, C., & Carle, R. (2003). A new process for the combined recovery of pectin and phenolic compounds from apple pomace. *Innovative Food Science & Emerging Technologies, 4*(1), 99–107.

Singelton, V. L., Orthofer, R., & Lamuela-Raventos, R. R. (1999). Analysis of total phenols and other oxidation substrates and antioxidants by means of Folin–Ciocalteu reagent. *Methods in Enzymology, 299*, 152–178.

Singh, J., Upadhyay, A. K., Prasad, K., Bahadur, A., & Rai, M. (2007). Variability of carotenes, vitamin C, E and phenolics in Brassica vegetables. *Journal of Food Composition and Analysis, 20*(2), 106–112.

Stratil, P., Klejdus, B., & Kuban, V. (2006). Determination of total content of phenolic compounds and their antioxidant activity in vegetables – Evaluation of spectrophotometric methods. *Journal of Agricultural and Food Chemistry, 54*(3), 607–616.

Szeto, Y., Tomlinson, B., & Benzie, I. F. F. (2002). Total antioxidant and ascorbic acid content of fresh fruits and vegetables: Implications for dietary planning and food preservation. *British Journal of Nutrition, 87*(1), 55–59.

Thaipong, K., Boonprakob, U., Crosby, K., Cisneros-Zevallos, L., & Hawkins Byrne, D. (2006). Comparison of ABTS, DPPH, FRAP, and ORAC assays for estimating antioxidant activity from guava fruit extracts. *Journal of Food Composition and Analysis, 19*(6–7), 669–675.

Tsao, R., & Yang, R. (2003). Optimization of a new mobile phase to know the complex and real polyphenolic composition: Towards a total phenolic index using high-performance liquid chromatography. *Journal of Chromatography A, 1018*(1), 29–40.

Vanamala, J., Cobb, G., Turner, N. D., Lupton, J. R., Yoo, K. S., Pike, L. M., et al. (2005). Bioactive compounds of grapefruit (Citrus paradisi Cv. Rio Red) respond differently to postharvest irradiation, storage, and freeze drying. *Journal of Agricultural and Food Chemistry, 53*(10), 3980–3985.

Whale, S. K., & Zora, S. (2007). Endogenous ethylene and color development in the skin of 'Pink Lady' apple. *Journal of the American Society for Horticultural Science, 132*(1), 20–28.