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Effect of different cooking regimes on rhubarb polyphenols

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ABSTRACT

Polyphenolic components, such as anthraquinones and stilbenes, from species of the genus *Rheum* have been shown to have a range of bioactivities relevant to human health. This paper outlines the polyphenolic composition of edible petioles of garden rhubarb (*Rheum rhapontigen*) and describes the effects of common cooking methods on total polyphenolic content, anthocyanin content and total antioxidant capacity.

Most cooking regimes (fast stewing, slow stewing and baking) except blanching increased total polyphenol content and overall antioxidant capacity, compared to the raw material. The patterns of anthocyanin content and total polyphenol content between the different cooking regimes suggested a balance between two processes; cooking facilitated the release of polyphenol compounds from the rhubarb but also caused breakdown of the released compounds.

Baking and slow stewing offered the best maintenance of colour through preservation of anthocyanin and the highest antioxidant capacity. Baking for 20 min provided well-cooked rhubarb with the highest antioxidant capacity and the highest anthocyanin content, which is important for the aesthetic quality of the dish.

Liquid chromatography–mass spectrometric (LC–MS) analysis putatively identified over 40 polyphenol components in raw rhubarb, including anthraquinone, stilbene, anthocyanin and flavonol derivatives. Baking caused selective effects on the stability of the different polyphenol components. Initially, the yield of all components increased but there was a drastic decline in the relative stability of anthraquinone aglycones with increasing cooking time and initial evidence for the turnover of other anthraquinone derivatives was obtained.

1. Introduction

Species of the genus *Rheum* have been reported to be rich in polyphenol components, such as anthraquinones, stilbenes, flavonols and anthocyanins (Koyama, Morita, & Kobayashi, 2007), which may have bioactive effects (Zhou & Yu, 2006). Rhubarb species have been used in traditional Chinese medicine for thousands of years (Yang, 1998) and have been used in the treatment of gastrointestinal dysfunction, ulceration, inflammation, renal protection and as anti-microbial agents (Huang, Lu, Shen, Chung, & Ong, 2007).

Anthraquinones commonly found in medical rhubarb extracts, such as emodin, rhein and chrysophanol, may be partly responsible for these effects and have been shown to have beneficial effects in model systems for neurobehavioral deficits associated with schizophrenia (Mizuno, Kawamura, Takei, & Nawa, 2008), diabetes (Zheng, Zhu, Li, & Liu, 2008), cancers (Chen, Hsieh, Chang, & Chung, 2004; Yu, Liu, Cheng, Hu, & Hou, 2008), cardiovascular disease (Liu et al., 2008; Zhi-Heng, Ming-Fang, Shuang-Cheng, & Pui-Hay, 2008), symptoms associated with menopause (Möller et al., 2007) and inflammation (Ding et al., 2008).

Stilbene derivatives from rhubarb have also been shown to have biological effects (e.g., Park, Choo, Yoon, & Kim, 2002) and related resveratrol derivatives from other plant sources have received much attention (Baur & Sinclair, 2006). Anthocyanins and flavonols also found in rhubarb may have biological effects (Hertog & Hollman, 1996; Prior & Wu, 2006; Wang & Stoner, 2008) in their own right.

However, most studies have focused on root samples of *Rheum* species used in traditional Chinese, or Korean, medicine (e.g., *Rheum emodi, Rheum officinale, Rheum undulatum* and *Rheum* tanguticum [Pussa, Raudsepp, Kuzina, & Raal, 2009]) and little is known about the potential bioactive components in edible petioles of cultivated garden rhubarb (*Rheum rhapontigen*). Although rhubarb can be eaten raw, most rhubarb in the United Kingdom and Europe is cooked before consumption. In this paper, we assess the effects of cooking regimes that mimic typical cooking procedures on the fate of potential bioactive components of rhubarb.

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2. Materials and methods

2.1. Plant material and cooking conditions

Rhubarb (*Rheum rhaponticum* cultivar Crimson Crown) was grown under typical forced growing conditions and was obtained from Oldroyd & Sons Ltd., Rothwell, Leeds, UK. This is top-quality premium rhubarb and was selected due to its ruby-red colour and slender straight stems. The rhubarb was washed to remove adhering soil and dried. The stems were cut into one-inch lengths. The sample was well mixed to ensure that each cooked sample included a random mix of tissue from the length of the stalk, as it was possible that the source of material could influence polyphenol content.

To mimic relevant procedures in the preparation of rhubarb, we developed four cooking regimes. The first of these was blanching (A), which was selected as it is common for rhubarb to be blanched prior to frozen storage. Slow (B) and fast (C) cooking procedures were included to mimic either gentle, low temperature stewing (less than 80 °C) or faster hotter stewing (100 °C). Baking (D) at 180 °C was also included as a cooking regime as rhubarb is often baked from raw in pies, etc. Raw rhubarb was used as a control. The cooking regimes used 115 g of rhubarb with 200 ml water and 15 g of caster sugar, and were based on scaled-down versions of published recipes (e.g., Smith, 1992). The exceptions were the raw samples to which no water or sugar was added and the blanched sample, where no sugar was added and the blanching water was discarded. The rhubarb used in this study was picked, shipped, cooked and frozen all within the same day. The samples were delivered frozen to the Scottish Crop Research Institute for analysis.

(A) *Blanching:* 115 g of rhubarb were covered with 200 ml of boiling water (100 °C) for 5, 10, 20 and 30 min.

(B) *Slow cooking:* 115 g rhubarb were cooked with 200 ml water and 15 g of sugar to 60 °C and then cooked on the hob at its lowest setting (70–80 °C) for 2, 5, 10, and 20 min.

(C) *Fast cooking:* 115 g rhubarb were cooked with 200 ml boiling water and 15 g of sugar. The mixture was brought to the boil rapidly (100 °C) and simmered at this temperature for 2, 5, 10 and 20 min.

(D) *Baking:* 115 g rhubarb were placed in a three-inch cruet dish with 200 ml of water and 15 g sugar. The dish was covered in tin foil was placed in a pre-heated oven at 180 °C for 5, 10, 20 and 30 min.

Raw control rhubarb: 115 g of uncooked chopped rhubarb were vacuum-packed and frozen at −20 °C.

2.2. Extraction procedure

The rhubarb samples were thawed and washed out of their vacuum bags with a fixed volume of ice-cold ultra-pure water (UPW).

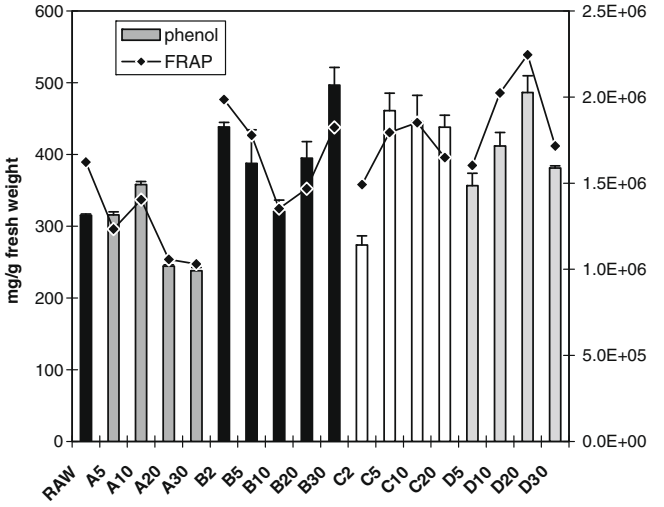

Fig. 2. Antioxidant capacity of cooked rhubarb samples. Values are averages of triplicates assay ± standard errors.

In turn, each sample was placed in a pre-cooled Waring blender. An equal volume of acetonitrile containing 0.2% formic acid was added to the rhubarb sample, to make a final extractant of 50% acetonitrile containing 0.1% formic acid, which has previously been shown to be optimal for the extraction of polyphenols from raspberries (Stewart et al., 2007). The rhubarb samples were homogenised (5×30 s at full power). The pulp was removed and strained through a nylon filter with a 50 μm pore size. The final recovered volume was recorded for yield determination.

The addition of 0.1% formic acid stabilised the extracted components and the addition of 50% acetonitrile at low temperatures precipitated soluble pectin and pulp particles, which were removed, as this could affect the later assays. Re-extraction of the pulp did not exceed 5% of the total phenol content of the initial extract.

2.3. Phenol and anthocyanin content and antioxidant capacity

Sub-samples of the extracts were centrifuged at 5000*g* for 15 min at 4 °C. Total anthocyanin concentration was estimated by a pH differential absorbance method (Deighton, Brennan, Finn, & Davies, 2000). The absorbance value was related to anthocyanin content, using the molar extinction coefficient calculated for cyaniding 3-*O*-glucoside (purchased from ExtraSynthèse Ltd., Genay, France). Phenol content was measured using a modified Folin–Ciocalteau method (Deighton et al., 2000). Phenol contents were esti-

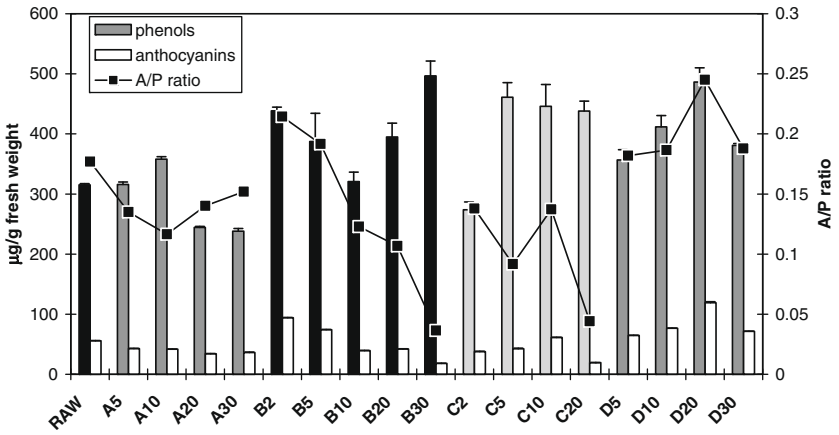

Fig. 1. Polyphenol and anthocyanin content of cooked rhubarb samples. Values are averages of triplicates assay ± standard errors.

mated from a standard curve of gallic acid. The antioxidant potentials of the samples were measured using the ferric reducing ability of plasma (FRAP) and Trolox equivalent antioxidant capacity (TEAC) protocols (Deighton et al., 2000). All assays were carried out in triplicate and values shown are means ± standard errors.

2.4. Liquid chromatography–mass spectrometry

Samples were also prepared for compositional analysis by liquid chromatography–mass spectrometry to examine the profile of components following the cooking regimes. Initial attempts to directly analyse the original extracts were prevented by poor separation of components, perhaps due to retention of pectin or sugars in the samples, so extracts were prepared using solid phase extraction (SPE). Aliquots were acidified by the addition of equal volumes of 0.2% formic acid in UPW then centrifuged at 15,000*g* for 10 mins. The supernatant was applied to C18 SPE units (Strata C18-E, GIGA units, Phenomenex Ltd., Macclesfield, UK) pre-washed in 0.1% (v/v) formic acid in acetonitrile and then equilibrated in 0.1% (v/v) formic acid in UPW. Unbound material, which contained sugars, organic acids and pectins, was discarded. After extensive washes with UPW, the polyphenol-enriched bound extracts were eluted with successive volumes of acetonitrile, acetone and ethyl acetate. We found that this elution procedure was most effective in recovering the greatest diversity of components (results not shown). After checking phenol contents, the C18-bound extracts were evaporated to dryness in a Speed-Vac (Thermo Fisher, Basingstoke, UK). The supernatants were re-suspended to 1 mg/ml gallic acid equivalents of phenol content and then analysed on an LCQ-DECA system, comprising Surveyor autosampler, pump, photodiode array detector (PDAD), and a ThermoFinnigan iontrap mass spectrometer. The PDAD scanned three discrete channels at 280, 365, and 520 nm. Samples were eluted with a gradient of 5% acetonitrile (0.1% formic acid) to 100% acetonitrile (0.1% formic acid) on a C18 column (Synergi Hydro C18 with polar end capping, 4.6 mm × 150 mm, Phenomenex Ltd.) over 60 min at a rate of 400 μl/min. The LCQ-DECA liquid chromatography–mass spectrometer was fitted with an electrospray ionisation interface, and the samples were analysed in positive- and negative-ion mode. There were two scan events: full-scan analysis followed by data-dependent MS/MS of the most intense ions. The data-dependent MS/MS used collision energies (source voltage) of 45% in wide-band activation mode. The MS detector was tuned against cyaniding 3-*O*-glucoside (positive mode) and against quercetin 3-*O*-glucoside (negative mode). Once components had been putatively identified by their relative retention, their PDA spectra and their mass spectral properties, the amount of specific components was estimated using the peak area calculated under the specific *m/z* value for each molecular species, as defined by the software associated with the mass spectrometer (Xcalibur, ThermoFinnigan). This method gives a reasonable and internally comparable estimate of content even when peaks were not completely separated.

3. Results and discussion

In general, the total polyphenol content was greater in samples of cooked rhubarb than the raw rhubarb (Fig. 1). The highest polyphenol levels were observed after slow cooking for 30 min, closely followed by baked rhubarb at 20 min (Fig. 1; B30, D20). Blanching seemed less effective as the polyphenol levels dropped after 20 and 30 min (Fig. 1; A20 and A30) but it is it is likely that some components were lost as the blanching water was not retained. Although there was a dip in the total polyphenol content at 10 min slow cooking (Fig. 1), the general pattern in cooked samples was an increase followed by a levelling out of total polyphenol content.

The red-coloured anthocyanins gave a visual representation of the effect of the different cooking regimes. The anthocyanins represented a sub-fraction of 1/5 the total polyphenol content of the raw rhubarb (Fig. 1). During blanching, there was a reduction of the anthocyanins with increased cooking time but this reduction was less dramatic than that of the total polyphenol content. Under the slow cooking regime, the anthocyanin content was higher than that of the raw sample after 2 and 5 min treatment (Fig. 1; B2 and B5) but thereafter dropped below the raw levels. Under fast cooking conditions, the anthocyanin content increased from 2 to 10 min treatment (Fig. 1; C2–C10) but even at its maximum value (C10) it was never significantly higher than the raw sample. Under baking conditions, the anthocyanin content was above raw levels after

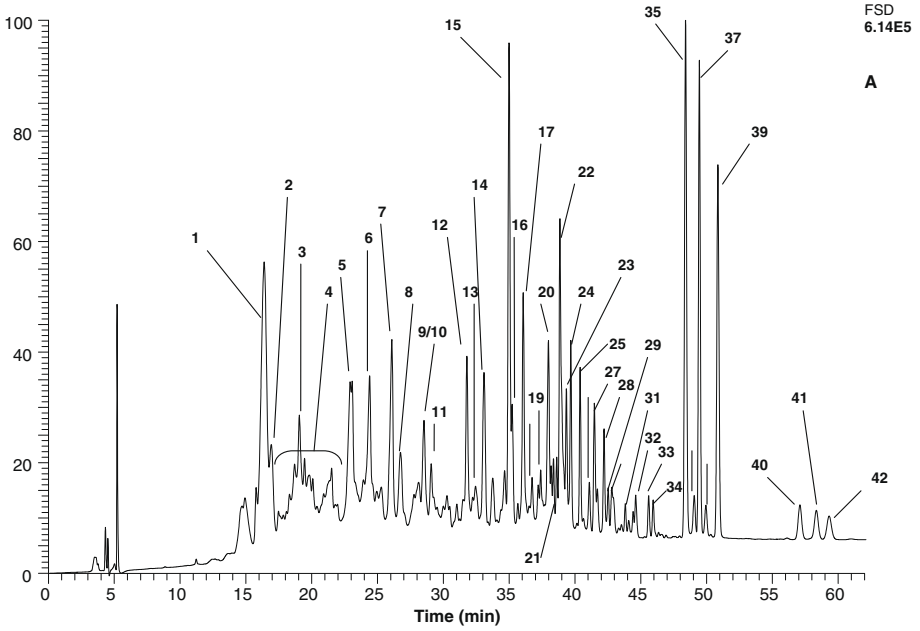

Fig. 3. LC–MS trace of raw rhubarb extract. Annotated peaks are discussed in Table 1. FSD, full scale deflection.

5 min cooking and continued to increase until 20 min (Fig. 1; D series).

These observations fit with the idea of a balance between release of components from the rhubarb upon cooking and the breakdown of the released compounds. For example, the low levels of anthocyanins in the fast cooked samples suggest a shift in the balance towards degradation whereas the accumulation of anthocyanins in the baked samples suggests continued extraction with reduced degradation. This trend is illustrated by comparison of the total polyphenol and anthocyanin contents as a ratio (Fig. 1). The total polyphenol content was not so greatly affected by the increased cooking times as the anthocyanin content (Fig. 1; see B30, C20 and D30), probably because the anthocyanins break down to non-coloured phenolic products, which also react with the Folin's reagent. Initially, other components also probably break down to other phenolic products, which would explain the noted maintenance of phenol content at longer cooking times.

The antioxidant capacity of the rhubarb samples was measured using the FRAP and TEAC methods. However, both the FRAP values and TEAC values largely tracked the phenol profiles so only the FRAP values are shown for clarity (see Fig. 2). The correlation between these antioxidant measurements and the Folins assay has been described before (Prior, Wu, & Schaich, 2005), as they measure essentially related redox parameters. Only the 2 min slow-cooked sample (B2) and the mid-time baked samples (D10 and D20) had FRAP values substantially above that of the raw rhubarb. These peaks in antioxidant capacity correspond to some of the highest levels of total phenol content and the B2 and D20 samples had the highest anthocyanin content.

The raw rhubarb sample contained 42 components which could be putatively identified by comparison of their retention times, PDA spectra and mass spectral data (Fig. 3 and Table 1) with previous reports on rhubarb roots (Fuh & Lin, 2003; Han et al., 2008; Komatsu et al., 2006; Ye, Han, Chen, Zheng, & Guo, 2007) or by comparison with equivalent components in berry samples (Maatta-Riihinen, Kamal-Eldin, Matiila, Gonzalez-Paramas, & Torronen, 2004). However, comparison to previous work is difficult because many of the previous papers have focused on species other than edible rhubarb (e.g., Han et al., 2008; Ye et al., 2007, which show considerable species-to-species variation in composition), have exclusively used rhubarb roots or have analysed special medicinal rhubarb preparations or sub-fractions (Komatsu et al., 2006). However, Pussa et al. (2009) compared roots and petioles of edible rhubarb (*R. rhaponti-gen*) and identified many of the same components but with some differences possibly due to differences, in cultivars or extraction procedures.

Table 1
Putative identification of components in raw rhubarb.

Peak No.	Retention time	PDA maxima	*m/z* [M−H]	MS^2	Putative identification
1	16.29	515, 280	**595.0**$^+$, 287.2	**287.2**, 449.0	Cyanidin rutinoside
2	16.83	515, 280	**449.0**$^+$, 287.2	287.2	Cyanidin hexose
3	18.96	325	**301.1**, 165.1	165.1	UK
4	17–22	ND	Multiple	NA	Proanthocyanidins
5	22.77	355	**610.9**$^+$, 303.2	303.2	Quercetin rutinoside
6	24.30	350	**464.9**$^+$, **479.2+**, 303.2	303.2	Quercetin hexose/quercetin glucuronide
7	25.99	325	**419.0**, 257.1	257.1	Rhapontigen hexose
8	26.68	355	**448.9**$^+$, 303.2	303.2	Quercetin rhamnose
9	27.49	ND	**419.0,** 257.1	257.1	Rhapontigen hexose
10	28.43	425, 285	**431.2**, 269.2	269.2	Aloe emodin-hexose
11	28.98	325	**693.1**	**517.1**, 499.0, 265.0	UK
12	31.69	425, 285	**473.1**, 269.2	269.2	Aloe emodin acetyl hexose
13	32.52	ND	**406.9**, 245.2	245.2	Torachyrosone hexose
14	32.99	425, 285	**431.2**, 269.2	269.2	Emodin-hexose
15	34.89	425, 280	517.0, **473.2**, 269.2	269.2	Aloe emodin acetyl hexose
16	35.13	325, 280	**449.0**, 245.2	245.2	Torachyrosone acetyl hexose
17	35.97	345	**489.1**, 285.2	285.2	Hydroxy emodin acetyl hexose
18	36.63	330, 280	**458.2**, 254.2	254.2	Chrysophanol acetyl hexose
19	37.29	330, 280	**458.2**, 254.2	254.2	Chrysophanol acetyl hexose
20	37.88	350–400	**671.2**, 416.1, 254.2	**416.1**, 254.2	Dimer of emodin + hexose
20	38.51	350	**713.1**, 458.2, 254.2	**458.2**, 254.2	Dimer of emodin + acetyl hexose
21	38.75	320	**757.2**, 713.1, 458.2, 254.2	**713.2**, 671.2	Dimer of emodin + malonyl hexose
22	38.80	ND	**985.1,** 839.1	839.2, 823.2	UK
23	39.25	345	**713.2**, 671.2, 458.2, 254.2	508.9, **458.2**, 254.1	Dimer of emodin + acetyl hexose
24	39.58	350	**757.2**, 713.1, 458.2, 254.2	**713.1**, 502.0, 458.2,	Dimer of emodin + malonyl hexose
25	40.29	350	**757.2**, 713.1, 458.2, 254.2	**713.1**, 502.0, 458.2,	Dimer of emodin + malonyl hexose
26	40.99	350	**671.2**, 458.2, 416.2, 254.2	**509.1**, 416.2, 254.2	Dimer of emodin + Glc
27	41.37	350	**757.0**, 713.1, 502.0, 458.2, 254.2	**713.1**, 502.0, 458.2	Dimer of emodin + malonyl hexose
28	42.11	350	**757.0**, 713.1, 502.0, 458.2, 254.2	**713.1**, 502.0, 458.2	Dimer of emodin + malonyl hexose
29	42.41	350	771.1, **727.1**, 685.1, 254.2	**523.2**, 458.2, **254.2**	Dimer of rhein + emodin + acetyl hexose
30	42.71	350	771.1, **727.1**, 685.1, 254.2	**523.2**, 458.2, **254.2**	Dimer of rhein + emodin + acetyl hexose
31	43.72	350	771.1, **727.1**, 685.1, 254.2	**523.2**, 458.2, **254.2**	Dimer of rhein + emodin + acetyl hexose
32	44.52	360	**683.0**, 547.1, 267.2, 254.1	**683.0**, **547.0**, 427.1, 267.0	Unknown dimer
33	45.55	360	**683.0**, 547.1, 267.2, 254.1	**683.0**, **547.0**, 427.1, 267.0	Unknown dimer
34	45.84	365	**683.0**, 547.1, 267.2, 254.1	**683.0**, **547.0**, 427.1, 267.0	Unknown dimer
35	48.30	440, 285	**269.2**	269.2, 225.2	Aloe emodin
36	48.96	395, 270	**245.2**, 230.1, 215.2	245.1, **230.1**, 215.2	Torachyrosone
37	49.35	360	**254.2**, 509.1	254.2	Chrysophanol
38	49.84	360	**285.2**	285.2, **257.1**, 242.2	Hydroxy emodin
39	50.76	360	**254.2**, 509.1	254.2	Chrysophanol
40	56.99	360	**523.0**, 254.2	254.2	Dimer of chrysophanol + emodin
41	58.24	360	**523.0**, 254.2	254.2	Dimer of chrysophanol + emodin
42	59.21	435, 285	ND	ND	UK

UK, unknown; ND, not determined. Figures in bold represent the main ion in the *m/z* spectra and the main fragment ion in the MS^2 spectra. It also represents the ion chosen for fragmentation. Figures with superscript + were obtained with positive mode ionisation.

Four late-eluting peaks (peaks 35–39; Table 1) were putatively assigned as the anthraquinone aglycones (aloe emodin, torachyrosone, chrysophanol and hydroxy emodin; Komatsu et al., 2006) and another two as dimers of anthraquinone aglycones. Other peaks (peaks 7, 9 and 10–19; Table 1) were putatively assigned as acetyl or malonyl hexose derivatives of rhapontigen, aloe emodin, emodin, torachyrosone, hydroxy emodin and chrysophanol (Pussa et al., 2009). No sennoside dimer components as described by Ye et al. (2007) could be identified, although fifteen peaks (peaks 20, 21, and 23–34; Table 1) were putatively assigned as structurally related acetyl or malonyl hexose derivatives of other dimers. Indeed, the absence of sennoside derivatives has been noted as characteristic of subsection *deserticola* of the *Rheum* family (Han et al., 2008).

There was little evidence of stilbenes such as the resveratrol, pterostilbene or piceatannol derivatives identified by Pussa et al. (2009) in *R. rhapontigen* petioles and by other groups in roots of other *Rheum* species (Ye et al., 2007). However, small amounts of piceatannol-hexose (m/z = 405 and MS^2 = 243) and pterostilbene hexose and pterostilbene acetyl hexose (m/z = 459 and 417, respectively, with a common aglycone MS^2 = 255) could be detected by searching the data at the relevant m/z values, usually under other more abundant peaks. These components were more easily detected, but still as minor components, in acetonitrile extracts from the C18 SPE columns suggesting that they had been overwhelmed by other components (results not shown). No resveratrol derivatives were identified in our extracts.

In the early eluting components, we found substantial amounts of two anthocyanins (cyanidin 3-*O*-rutinoside and cyanidin 3-*O*-glucoside; Wrolstad & Heatherbell, 1968) and evidence for the presence of a range of proanthocyanidins and quercetin derivatives.

However, after taking into account reservations about the identification of the components, it is possible to track the relative sur-

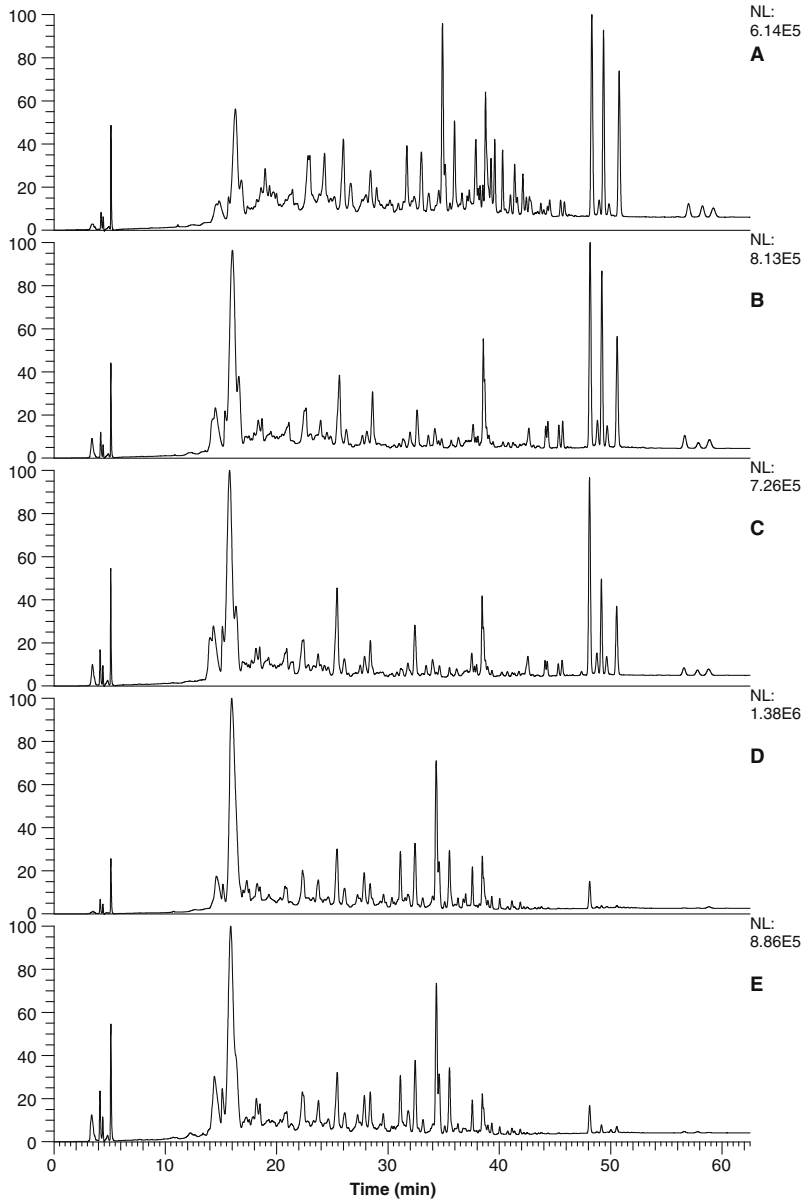

Fig. 4. Effect of baking on rhubarb polyphenol composition. The FSD (full scale deflection) is given in the top right corner of each trace. Each trace shows the absorbance at 280 nm. (A) the raw extract, (B) the baked sample at 5 min, (C) at 10 min, (D) at 20 min and (E) at 30 min. Each trace is the result of injection of 20 g gallic acid equivalents (GAE) phenol content.

vival of these components during cooking (Fig. 4). The samples were analysed at equivalent phenol contents, which highlights qualitative changes in relative abundance of components but does not allow comparisons of the total level of the components. Nevertheless, certain trends can be discerned. There is a dramatic decrease in the relative amounts of the anthraquinone aglycones between 5 and 10 min baking (Fig. 5A), which is accompanied by a decrease in the levels of the anthraquinone glycoside derivatives (Fig. 5B) and the putative anthraquinone dimer derivatives (Fig. 5C). The apparent recovery in the abundance of certain anthraquinone derivatives at 20 min (e.g., peak 15; assigned to aloe emodin acetyl hexose) may be due to increased extraction from the tissue or as breakdown products of the dimeric anthraquinone components. Nevertheless, it would seem that, at least part of, this apparent increase is in compensation for the drastic reduction in the content of the anthraquinone aglycones. This compensation effect can also be seen in the increased level of anthocyanin components at 20 min (Fig. 5D) but the underlying pattern of anthocyanin content (increase till 20 min then decline) still mirrors the total anthocyanin content measurements (Fig. 1).

It is clear that cooking under relevant domestic regimes caused different effects on the different classes of polyphenols. Available anthocyanin content was increased by most cooking procedures except fast stewing, and at 20 min baking, the rhubarb was both suitably cooked and had the highest anthocyanin content and the highest antioxidant capacity (Figs. 1 and 2). Therefore, the maintenance of red colouration during cooking would be both aesthetically pleasing and maximise antioxidant capacity.

However, although baking caused initial increases in the content of some anthraquinone aglycones, baking until suitably cooked (20 min) led to a great decrease in their content. There is a suggestion that the anthraquinone dimer derivatives may have broken down to form anthraquinone monomer glycosides (compare Fig. 5B and C) but this would require in-depth studies of the dynamics of the process. In addition, the noted increase in abundance of the apparent dimer components with ions at *m/z* 683 after 5 min baking (Fig. 5B) cannot readily be explained, unless these components are released from the matrix or they are breakdown products of other components.

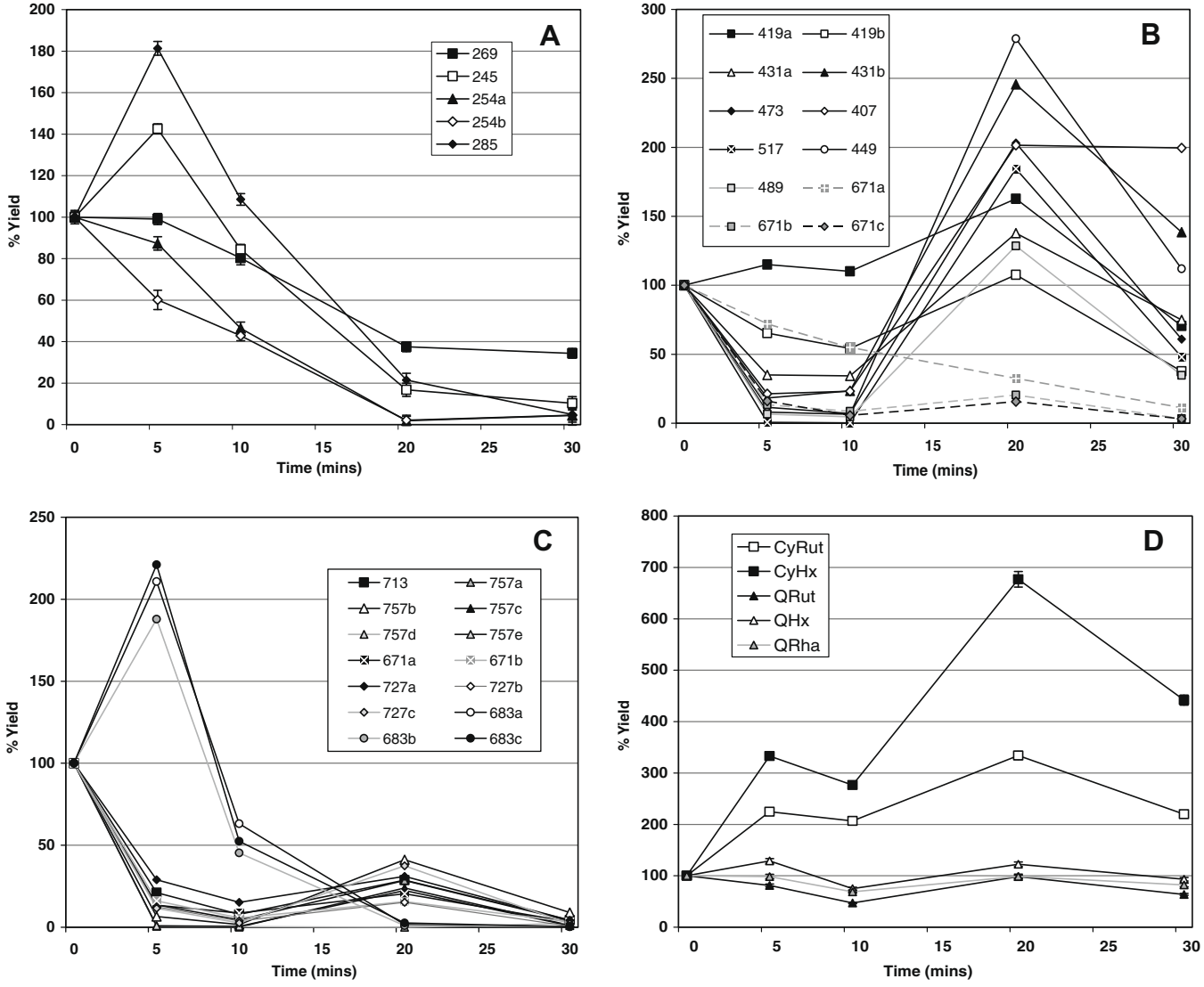

Fig. 5. Effect of baking on rhubarb polyphenol constituents. All values are obtained from peak areas from triplicate runs ± standard errors then converted into % raw figures. (A) displays the anthraquinone aglycones, (B) displays the anthraquinone hexose derivatives, (C) displays the anthraquinone dimer derivatives and (D) displays the anthocyanin and flavonol derivatives.

4. Conclusions

Edible rhubarb contains a diverse range of polyphenol components which offer a total phenol content and antioxidant capacity lower than raspberry (Deighton et al., 2000) and other berries but apparently higher than many vegetables (Zhou & Yu, 2006). The increases in antioxidant capacity after cooking are probably the result of a balance between enhanced release of polyphenols from the plant matrix and degradation of the released components. In addition, as most polyphenols will, at least initially, degrade to other polyphenol components, the antioxidant capacity of cooked samples remained higher than the raw samples.

The rhubarb samples had a polyphenol composition that was different from previous reports, which mainly focused on Oriental medicinal rhubarb preparations from species other than *R. rhapontigen*. However, a range of anthraquinone and stilbene derivatives were detected, which were similar to those previously described. Sennosides, which could have been expected from previous findings, were not identified, but a range of structurally-similar dimer derivatives were identified, as well as other anthraquinone derivatives, which have been shown to have potent biological activities.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.foodchem.2009.07.030.

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