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STUDY OF BIOACTIVE COMPOUND CONTENT IN DIFFERENT ONION SECTIONS

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ABSTRACT

BACKGROUND: The food industry produces a large amount of onion waste, making it necessary to search for possible ways for their utilization. One way could be to use these 'waste' onions as a new and natural source of high-value functional ingredients, due to the presence of bioactive compounds in onion, which present health benefits. The aim of this work was to provide information on the onion bulb (cv. Recas) and its sections in order to evaluate its potential use as a functional ingredient rich in fructooligosaccharides (FOS), flavonoids and alk(en)yl cystein sulphoxides (ACSOs), as well as good antioxidant activity.

RESULTS: The results showed that onion bulbs cv. Recas presented a moderate content of fructans, similar to other Spanish onion varieties, and these compounds were mainly found in the inner fleshy scales. Low ACSO content indicated that cv. Recas is a mildly pungent variety with the highest concentrations also being found in the inner fleshy

scales. However, cv. Recas presented a high level of flavonoids and therefore potential antioxidant activity, mainly in outer sections, like the brown skin.

CONCLUSION: In conclusion, bioactive compounds are distributed throughout the bulb, and therefore, wastes could be used to generate functional ingredients with important potential health promoting properties.

Keywords: ACSOs, fructans, fructooligosaccharides, flavonoids, onion, sections.

INTRODUCTION

Onions (*Allium cepa* L.) are the second most important horticultural crop worldwide, after tomatoes, with current annual production around 66 million tonnes (FAO, 2009). Over the past 10 years, onion production has increased by more than 25 %. Onion is a vegetable widely consumed in Europe, it is consumed uncooked in sandwiches and salads, but is also often cooked before eating. Moreover, an increase in demand for processed onions has led to an increase in waste production. Accordingly more than 500,000 tonnes of onion waste are produced annually in the European Union, mainly from Spain, UK and Holland (Waldron, 2001) and are increasing year on year. The main onion wastes include onion skins generated during industrial peeling, two outer fleshy scales and roots, and undersized, malformed, diseased or damaged bulbs. Due to the onions characteristic aroma, onion waste is not suitable for fodder in high concentrations (Schieber, 2001). Therefore onion waste could be used as a source of food ingredients, since it has been reported that onion is a potent cardiovascular and anticancer agent, with hypocholesterolemic, antithrombotic and antiplatelet activity, and antioxidant effects, besides the antiasthmatic and antibiotic effects (Moreno *et al*, 2006). At present, there is a considerable debate over the specific components responsible for

51 the health benefiting effects of onions. Two main groups of chemical compounds have
52 been proposed: flavonoids and alk(en)yl cystein sulphoxides (ACSOs) (Mogren *et al.*,
53 2007).
54 Onion composition is variable and depends on cultivar, stage of maturation,
55 environment, agronomic conditions, storage time and bulb section (Abayomi *et al.*,
56 2009; Rodriguez *et al.*, 2009; Downes et al., 2010a). Water makes up the majority
57 (80%–95%) of the fresh weight of onion. Up to 65 % or more of the dry weight may be
58 in the form of non-structural carbohydrates which include glucose, fructose, sucrose and
59 fructooligosaccharides (FOS) which are fructans of a low degree of polymerisation
60 (Davis *et al.*, 2007). The main FOS in onion bulbs are kestose (GF2), nystose (GF3) and
61 fructofuranosylnystose (GF4) (Jaime *et al.*, 2001; Vågen and Slimestad, 2008). Helath
62 benefits of these carbohydrates have been widely reported in the past few years
63 (Roberfroid, 2001) and their prebiotic effect demonstrated in an acceptable number of
64 studies (Playne et al 2003).
65 Moreover, onion is one of the major sources of dietary flavonoids in many countries (Ly
66 *et al.*, 2005). Two flavonoid subgroups are present in onion; anthocyanins, which impart
67 a red/purple colour to some varieties and flavonols such as quercetin and its derivatives
68 which may play a role in the production of yellow and brown compounds found in the
69 skins of many other varieties (Downes *et al.* unpublished). In recent literature, quercetin
70 4'-glucoside and quercetin 3,4'-diglucoside are in most cases reported as the main onion
71 flavonols of the flesh (Roldán-Marín *et al.*, 2009; Downes *et al.*, 2010a) whereas onion
72 skins contain higher concentrations of quercetin aglycon (Downes et al., 2009).
73 Quercetin is known for its antioxidant and free radical scavenging power and its
74 capability in protecting against cardiovascular disease (Bonaccorsi *et al.*, 2008).

Furthermore, quercetin exhibits anticancer, antiinflamatory and antiviral activity (Caridi *et al.*, 2007).

The ACSOs are the flavour and aroma precursors, which, when cleaved by the enzyme alliinase, generate the characteristic odour and taste of onion. Four ACSOs have been identified in *Allium*, and the flavour variation among species is due to differences in ACSO composition and concentration (Randle *et al.*, 1995). The three naturally occurring ACSOs in onion are trans-(+)-S-(1-propenyl)-l-cysteine sulphoxide (PECSO), which is normally found in the highest concentration and gives rise to the compound responsible for the lachrymatory effect, and (+)-S-methyl-l-cysteine sulphoxide (MCSO) and (+)-S-propyl-l-cys-teine of sulphoxide (PCSO), which are found in smaller amounts, or occasionally, in the case of PCSO, completely absent (Thomas and Parkin, 1994; Mallor & Thomas, 2008). *Allium* sulphur compounds have the ability to positively modify the antioxidant, apoptotic, inflammatory and cardiovascular systems in mammalian systems (Rose *et al.*, 2005).

The objective of this work was to determine the content of bioactive compounds and antioxidant activity in onion wastes emanating from industry and also in discarded whole onions in order to evaluate the potential use of onion waste as a source of bioactive compounds for its addition in a wide range of foodstuffs. Such information may be useful to food technologists for the potential exploitation of onion industry waste which could be used as functional food ingredients.

MATERIAL AND METHODS

Material

Onions cv. Recas were supplied by a Spanish onion producing industry (CEBACAT, Catalonia, Spain). Cv. Recas is a Valencia late cycle and long-day variety, which is

yellow, firm, with high density, and good storage capacity. The samples analyzed were not marketable onions, due to sprouting, damage in the outer scales, lost peel or below commercially acceptable size (< 45mm). From the 20 kg received, three batches of 10 onions were taken randomly. Onions were cut to obtain different sections similar to those generated in industrial peeling: top-bottom (~ 5-10 mm sliced off the top and bottom ends of the onion); brown dry outer skin; outer two fleshy scales and the remaining inner fleshy scales. In addition, the whole onion including all tissue types was analysed. The separated sections and whole onion were immediately frozen in liquid nitrogen after cutting and stored at -40 °C. Subsequently, samples were freeze-dried, milled and sieved (0.5 mm). All analysis was carried out in triplicate.

Dry Matter

Dry matter content was evaluated by drying samples to a constant weight at 55 °C in a vacuum oven

Non-structural carbohydrates extraction and determination

Non-structural carbohydrates were extracted according to Jaime *et al.* (2001). Freeze-dried samples (1 g ± 0.1 mg) was homogenized in 50 mL of 70 % (v/v) ethanol and immediately heated at 100 °C for 10 min. Subsequently, the mixture was centrifuged at 4000 rpm for 15 min and the supernatant decanted. The residue was extracted four extra times. All supernatants were pooled and vacuum evaporated at 30°C until dry. The concentrated sugars were redissolved in 50 mL of deionised water, and the solution stored at -20 °C until further determination of soluble carbohydrates. An extract aliquot was filtered by Sep-Pak cartridge and Millex HV13 filter (0.45 µm, Millipore, Billerica, MA, USA).

Fructose, glucose, sucrose and FOS were identified and quantified in the extract using Beckman Coulter LC125 HPLC system (Beckman Coulter, Brea, CA, USA) coupled to

125 Beckman 156 refractive index detector. The injection volume was 100 μL and the
126 separation occurred on an Aminex HPX-42C column (cationic ion exchanger, 0.78 x 30
127 m, Bio-Rad, Hercules, CA, USA). The column temperature was maintained at 85 °C
128 and deionised water was used as the mobile phase at a flow rate of 0.5 mL min^{-1}. The
129 data were presented in System Gold 8.0 software. Appropriate dilutions of a solutions
130 containing glucose, fructose and sucrose (Sigma, St Louis, MO) and 1-F-
131 fructofuranosylnystose, nystose and kestose (Wako Pure Chemical Industries, Ltd.,,
132 Osaka, Japan) were used as calibration standards.

133 **Total fructans**

134 Total fructans concentration in freeze-dried samples was measured using a fructan assay
135 kit (Megazyme, Co. Wicklow, Republic of Ireland) according to the manufacturer's
136 instructions (AOAC method 999.03, AACC method 32.32.) (Chope et al., 2006).

137 **Sulphur content**

138 Total sulphur content was determined using an elemental analyzer LECO CHNS-932
139 (LECO, S.L. St. Joseph, Michigan,USA). The microanalysis was based on sample total
140 oxidation through an instantaneous and complete combustion which converts the
141 sample into its combustion products (CO_2, H_2O, N_2 and SO_2).

142 S-alk(en)yl-L-cysteine sulphoxides (ACSOs) were determined according to Mallor and
143 Thomas (2008) with slight modifications. For ACSO extraction, 10 mg of freeze-dried
144 sample was added to 1 mL of 12:5:3 (v/v/v) methanol: chloroform: water and incubated
145 overnight at -20 °C. A 700 μL sample of the extract was transferred to a 1.5 mL
146 Eppendorf tube, to which 385 μL of water and 315 μL of chloroform was added. After
147 mixing, the phases were separated by centrifugation at 13,000 g for 30 s at room
148 temperature, and 790 μL of the upper phase was collected into an Eppendorf tube and

149 then freeze-dried. This extract was resuspended in 600 µL of 0.03M HCl and filtered
150 through a 0.2 µm filter.
151 HPLC analysis was carried out using an Agilent 1200 HPLC system (Agilent, Berks.,
152 UK) coupled to Agilent 1200 DA G1315B/G1365B photodiode array detector. The
153 injection volume was 15 µL and the separation occurred on a ZORBAX eclipse XDB-
154 C18 column (4.6 mm x 250 mm, 5µm) with an Agilent ZORBAX Eclipse XDB guard
155 column, 1.0 mm×17 mm (Part no. 5185-5921) at 25°C. The mobile phase was 0.03 M
156 HCl degassed by sonication and run at 0.6 mL min^{-1}. The data was presented in Agilent
157 ChemStation Rev. B.02.01 software and MCSO and PCSO were calibrated against
158 authentic standards and PECSO calibrated against allyl-cysteine-sulphoxide.
159 **Phenolic Compounds Extraction**
160 Phenolic compounds were extracted according to Downes *et al.* (2009) with slight
161 modifications. Freeze-dried samples were weighed (150 mg ± 0.5) and dissolved in 3
162 mL of 70:29.5:0.5 (v/v/v) methanol (analytical grade): water (Milli Q): HCl (analytical
163 grade). After mixing well, vials were placed in a shaking water bath at 35 °C for 90
164 min; samples had to be vortex every 15 min during the extraction to mix. When the
165 samples were cooled, they were filtered using a 0.2 µm filter. Extracts were stored in a
166 freezer at -20 °C until further analysis. This extracts were used to determine total
167 phenolics, total flavonoids, total antioxidant capacity and flavonols by HPLC
168 **Total phenolics, total flavonoids and total antioxidant capacity absorbance assays**
169 Total phenols and total antioxidant capacity were measured according to Terry *et*
170 *al.*(2007) and total flavonoids were determined according to Downes *et al*., (2010a)
171 **Flavonol Determination by HPLC**
172 Flavonols were determined according to Downes et al. (2010a) with slight
173 modifications. Extracts were analysed using an Agilent 1200 series HPLC system

(Agilent, Berks., UK). Flavonols were separated on a ZORBAX eclipse XDB-C18 column, 4.6mm x 150 mm, 5µm particle size (Part no. 993967-902), with an Agilent ZORBAX Eclipse XDB guard column, 1.0 mm×17 mm (Part no. 5185-5921). The mobile phase consisted of HPLC grade water with 0.5 g L^{-1} trifluoroacetic acid (TFA) (A) and acetonitrile with 0.5 g L^{-1} TFA (B). The gradient involved a linear increase/decrease in the amount of solvent B in A (%B): 0-6min, 5-25%; 6-14 min, 25-85%; 14-15 min, 85-5%. The flow rate was 0.8 mL min^{-1}. Samples (10 µL) were injected and the separation took place at 30°C. The flavonols eluted were detected with an Agilent 1200 DA G1315B/G1365B photodiode array at a wavelength of 370 nm. The data was presented in Agilent ChemStation Rev. B.02.01 software and quercetin and quercetin glucoside concentrations were calculated against authentic calibration standards (quercetin 3-glucoside, quercetin 4-glucoside, quercetin 3,4-diglucoside and quercetin; PlantChem, Sandnes, Norway), while for isorhamnetin glucosides, the equivalent quercetin glucoside standards were used.

Statistical analysis.

Mean comparison was performed using Duncan's multiple range test (DMRT) (Bender, 1989). Differences were considered to be significant at $P \leq 0.05$.

RESULTS AND DISCUSSION

Dry matter

Bulb dry matter (DM) content is an important quality parameter for the onion industry as it is related to other quality attributes, such as pungency, storage life, fructans and firmness. DM values of whole onion and onion sections are presented in Table 1. In agreement with Sinclair *et al* (1995), cv. Recas could be labelled as "fresh market" with regard to its DM content (88 g kg^{-1}). Onion sections reflected significant differences in

their dry matter contents; an increase was observed from inner tissues towards outer tissues. Thus, the fleshy tissues formed by inner scales and outer fleshy scales showed the smallest levels of dry matter, around 7%, whereas brown skin had the highest percentage around 50%. Dry weight of red and brown onion cvs. has found to be as high as 80% (Downes et al., 2009).

Non structural carbohydrates

The distribution of fructans and soluble sugars in Recas whole onion was studied (Table 2) Total non-structural carbohydrate (NSC) in whole onion was lower than that expected, generally, NSCs constitute a remarkably high proportion (60-80%) of the dry weight of onion bulbs (Rutherford and Whittle, 1982).. The NSCs consist of glucose, fructose, sucrose and low molecular weight fructans, in agreement with other authors (Jaime *et al.*, 2001; Chope *et al*., 2007; Davis et al., 2007). The main NSC component was glucose and the minor component of NSCs was fructans. Cv. Recas showed low fructan content and high free fructose levels; these results were similar to others varieties such as cv Grano de Oro or cv SS1 (Jaime *et al.*, 2001; Chope *et al*. 2007)), although they are different to other variety results, since fructans are cultivar dependent. The low fructan content found in cv. Recas could be related to its low dry matter content, since low dry matter onions often have little fructans and proportionally larger amounts of simple sugars, mainly glucose. Therefore, the NSC profile could be used to identify high or low dry matter onion varieties, (Kahane *et al.*, 2001; Chope et al., 2006). As well as being carbohydrate reserves, fructans are hydrolyzed to fructose to facilitate osmo-regulation as the bulb takes up water and expands during bulb development (Darbyshire and Henry, 1978; Jaime et al., 2001).

The NSC content of different onion sections were also analysed (Table 2). The NSC content in brown skin was not analyzed due to the small quantities found in previous

studies (Downes et al, 2009), which were not enough to be used as a fructan source (Jaime *et al.*, 2000). The highest concentration of NSCs and fructans were found in the inner scales, with a NSC profile very similar to the whole onion, since this section is the major contributor to the total weight of the bulb. However, there were differences between inner scales and the two outer scales with regard to NSC content. The two outer scales contained lower concentration of NSC components than inner, with sucrose and total fructans being the components present in lower proportions, whereas fructose and glucose contributed more to NSC content in the outer two scales than in inner. Furthermore, there is an increasing gradient of sucrose from the outer to the inner fleshy scales according to the results of Jaime *et al*. (2000) and a different spatial distribution of glucose within the bulb has been found according to Abayomi and Terry (2009). The glucose concentrations found herein were in the range of the low pungency onion cv. SS1 prior to storage. Onions cv. SS1 contained the highest concentrations of glucose in the inner scales (*ca.* 255 mg g^{-1} DW) and slightly lower concentrations in the outer second and third scale (*ca.* 225 mg g^{-1} DW) (Abayomi & Terry, 2009). Vertical spatial variation was also investigated in cv. SS1 with the top and bottom sections containing *ca.* 220 mg g^{-1} DW and the middle section *ca.* 260 mg g^{-1} DW. The discrepancy between these results and the results herein (Table 2) are probably due to several causes such as different cultivar, different extraction procedures and the different proportions of top and bottom sections sampled in each study. Only 5-10 mm were taken in this study but the top and bottom third of cv. SS1 was sampled after removal of the stem and base plate (Abayomi & Terry, 2009).

The NSC content in the top-bottom section was lower than in fleshy sections. Both free sugars and total fructans showed a drastic decrease in the top-bottom section with respect to fleshy scales. Moreover, top-bottom NSC profile was different to that found

249 in fleshy scales, since fructose constituted the main sugar and sucrose contribution was
250 higher than in fleshy scales.
251 A clear predominance of reducing sugars (fructose and glucose) against sucrose was
252 observed in every section, with the two outer scales being the section that showed the
253 highest ratio. In agreement, Salama *et al.* (1990) indicated higher levels of fructose and
254 glucose in the outer leaves of onion bulbs. On the other hand, a positive correlation was
255 observed between total fructan content and sucrose levels.
256 The FOS concentrations in whole onion and its sections are shown in Table 3. The
257 content of these FOS decreased as the degree of polymerisation increased, with
258 trisaccharides being the main component. The total FOS content of cv. Recas, as the
259 sum of kestose, nystose and 1-F-nystose, was lower than the total FOS found in other
260 varieties, but higher than that of cv. Grano de oro (Jaime *et al.*, 2001). Total FOS
261 accounted for 73 % of total fructans in whole onion; therefore, fructans in this variety
262 are composed mainly of FOS of low polymerization (DP3-DP5). According to the
263 literature, if the NSC content increases, the fructan degree of polymerisation also
264 increases (Jaime *et al*, 2000).
265 The FOS analysis of different onion sections showed that FOS were mainly located in
266 the inner part of the onion and in the two outer scales. Kestose was the main FOS
267 component in every section agreeing with Downes et al. (2010b). FOS contribution to
268 total fructans was among 73-87 % and. it was observed that the higher the fructan
269 content, the greater its degree of polymerisation
270 *Sulphur content*.
271 The sulphur (S) and flavour precursors (ACSOs) content was studied in onion and its
272 sections (Table 4). The highest S level was found in the inner scales and the lowest S
273 level was found in brown skin. Sulphur is incorporated into onion flavour precursors

(ACSOs) among other compounds. However, there was no correlation between total S content and flavour precursor content in agreement with other authors that showed that sulphur accumulation was poorly correlated with pungency in several onion cultivars (Randle *et al*., 1999; Chope *et al*., 2009). The S content in onion flavour precursors (total ACSOs) only represented 19 % of total S in onion and among 15-35 % in onion sections. The percentage of S-ACSOs in total S content suffered a decrease from inner to outer sections, although flavour precursors in brown skin accounted for almost 30 % of total S content.

In this study, only two ACSOs were detected, the (+)-S-methyl-l-cysteine sulphoxide (MCSO) and trans-(+)-S-(1-propenyl)-l-cysteine sulphoxide (1-PECSO). Propyl cysteine sulphoxide (PCSO) was not found in this variety. This is in agreement with the results found by other authors (Thomas and Parkin 1994; Yoo and Pike (1998); Bacon *et al.* 1999). The total flavour precursor content of whole onion was lower than the results found in other studies (Thomas and Parkin, 1994; Yoo and Pike, 1998). ACSO content showed good correlation with fructans and dry weight, generally low dry weight onions have low ACSO and fructan content (Chope *et al*., 2006).

On a dry weight basis, flavour precursor distribution within the bulb showed a decreasing gradient of concentration from inner to outer sections (Table 4), with the inner scales containing the highest content of ACSOs, The lowest level of precursors occurred in the brown skin suggesting that this material is of limited value as a source of flavour compounds.. This distribution is in agreement with Randle (1997), who indicates that there is a flavour gradient within the bulb. However, the distribution found in this study was in disagreement with Bacon *et al.* (1999), since they found in outer fleshy scales the highest content (on dry basis) of flavour precursors in three different varieties.

PECSO, a precursor of the lachrymatory factor, is the main flavour precursor in the whole bulb and its sections, accounting for 52-71 % of total precursors, these contributions were lower than those found in other varieties (Bacon *et al.*, 1999). A similar level was found in cv. Southport white glove (Randle *et al.*, 1995), although it was lower than the majority of other varieties (Yoo and Pike, 1998). The low levels and contribution of PECSO found in cv. Recas would indicate that it is a mildly pungent variety, since PECSO content is related to the onion pungency (Yoo and Pike, 1998). MCSO content was similar to the results found in other cultivars (Yoo and Pike, 1998). In general, PECSO is the main component in onion varieties accounting 90 % of onion flavour precursors (Thomas and Parkin, 1994; Yoo and Pike, 1998), even though there are some cases in which MCSO was the main component of onion flavour (Randle *et al.*, 1995). In cv. Recas, both components are in similar proportions in the whole bulb. The ratio of the various flavour precursors differs among cultivars and this ratio give rise to different taste and aroma (Randle,1997). When the bulb is cut the enzyme allinase converts ASCOs into volatile compounds such as pyruvate, 1-propenylsulfenic acid and ammonia. Abayomi & Terry (2009) measured the spatial distribution of pyruvate in cv. SS1. Prior to storage no difference in the spatial distribution of pyruvate in SS1 was recorded however after just 23 days storage (4°C in controlled atmosphere) the grouped inner scales contained double the concentration of pyruvate compared with the outer scales. This same trend was found herein for total S, MCSO, PECSO and total ACSO content suggesting pyruvate concentrations could be directly related to sulphur and ACSO content.

Phenolic content

322 Total phenolic, flavonoid and flavonol contents and antioxidant activity have been
323 studied in whole onion and onion sections (Table 5) Total flavonols are the sum of
324 individual flavonols obtained by HPLC shown in Table 6.
325 Total phenolic data reported in previous studies for onion bulb (Yang *et al.*, 2004;
326 Santas *et al.*, 2008) showed lower values than those obtained in this work. Regarding
327 the onion sections, a decrease was observed from outer to inner sections, with brown
328 skin being the section with the highest level of phenolics. This trend was found
329 previously in several varieties, although the present study showed higher level of
330 phenolic compounds in onion sections (Prakash *et al.*, 2007), Flavonoids showed the
331 same trend found in total phenolics. This distribution was also observed by Patil and
332 Pike (1995) and Gennaro *et al.* (2002). Whole onion flavonoids in this assay were
333 higher than flavonoids in other varieties (Yang *et al.* 2004). Flavonoids were the major
334 group of phenolic compounds, accounting for a high percentage of total phenolics in
335 onion sections. These results were in agreement with other authors (Yang *et al.*, 2004;
336 Santas *et al.*, 2008).
337 With regard to total flavonols, whole onion content was higher than those reported on
338 different onion varieties by Bonaccorsi *et al.* (2008). In relation to sections, the two
339 outer scales showed the highest level of flavonols, followed by top-bottom, with the
340 brown skin and inner fleshy scales containing the lowest amount of these compounds.
341 Flavonols were the main component of flavonoids in fleshy leaves, however, in top-
342 bottom and, especially, in brown skin flavonols represented a small percentage of total
343 flavonoids. The remaining flavonoids in these sections could be anthocyanins (Downes
344 et al., 2009).
345 With regard to individual flavonols measured using HPLC, six different compounds
346 were detected (Table 6) an aglycone; quercetin, and five flavonol glucosides The main

347 flavonols found in this study were quercetin 4'-glucoside and quercetin 3,4'-diglucoside
348 and the minor conjugates were isorhamnetin glucosides and quercetin 3'-glucoside,
349 these results were higher than in other varieties (Caridi *et al.* 2007). Main flavonols
350 accounted for over 80 % of total flavonols in whole onion, fleshy sections and top-
351 bottom, in agreement with the findings of Price and Rhodes (1997) and Rohn *et al.*
352 (2007). However, in other studies, these conjugates accounted for about 88 % or 90 %
353 (Lombard *et al.*, 2005; Bonaccorsi *et al.*, 2008). The main flavonol in whole onion was
354 quercetin 4'-glucoside, as well as in the top-bottom section and brown skin, whereas the
355 main flavonol in fleshy scales was the quercetin 3,4'-diglucoside. Our findings agreed
356 with Tsushida and Suzuki (1995) who reported that quercetin 4'-glucoside represented
357 the main quercetin glucoside in onions. The diglucoside:monoglucoside ratio was
358 different depending on the section studied; Lombard *et al.* (2005) previously reported a
359 similar ratio for whole onion. However, other authors obtained a higher diglucoside
360 content than monoglucoside (Price and Rhodes, 1997; Downes *et al.*, 2010a)
361 Discrepancies among the studies might be related either to cultivar differences or to
362 sample preparation prior to processing (Lombard *et al.* 2005).
363 Free quercetin was found mainly in outer sections, such as brown skin and top-bottom.
364 In the former this aglycone is the second major flavonol. The origin of higher quercetin
365 content in brown skin could be due to the hydrolysis of quercetin glucosides during peel
366 formation which suggests that quercetin could be involved in peel brown compounds
367 formation (Patil and Pike, 1995). The presence of free quercetin in the edible part of raw
368 onion was negligible, as other authors reported in previous studies.
369 Onion phenolic and sulphur compounds are among the onion bioactive compounds
370 contributing to onion antioxidant properties (Benkeblia, 2005). Antioxidant capacity
371 was determined in whole onion and each section (Table 5). Antioxidant capacity of

whole onion in the present study was higher than the antioxidant capacity observed by Santas *et al.* (2008) in several onion varieties. Moreover, the results showed that antioxidant capacity decreased from the outer to inner part of the onion. Thus, the best antioxidant activity corresponded to the brown skin, in agreement with Nuutila *et al.* (2003). This trend was also found by other authors (Ly *et al.* 2005; Prakash *et al.* 2007) in several onion varieties.

The high correlations between FRAP values and total phenolic content and total flavonoids (r= 0.98 and r= 0.99, respectively) confirm that flavonoids are the main compounds responsible for the antioxidant activity in onions sections according with other authors (Nuutila *et al.*, 2003; Santas *et al.*, 2008). Moreover, a high correlation between quercetin and FRAP values (r= 0.99) has been found, which indicates that quercetin content influences onion antioxidant activity. However, there was not a good correlation between quercetin or isorhamnetin glucosides and FRAP values, neither between total flavonols and FRAP values. Flavonols in the aglycone form are more active than when glycosilated, due to the presence of free hydroxyl groups (Rohn *et al.*, 2007; Santas el al., 2008). In consequence, brown skin and the top and bottom sections showed better antioxidant capacity than inner fleshy leaves. Results obtained showed that onion sections could be used as a potential source of bioactive compounds, with good antioxidant capacity.

CONCLUSION

In general, variations in the distribution of bioactive compounds in different onion sections were found in this study. Fructans and ACSOs were mainly located in inner fleshy scales and their content was moderate, although similar to some other varieties. On the other hand, flavonoids were located mainly in brown skin, but all the sections

and whole onion showed high concentrations and higher concentrations than other varieties. Furthermore, onions are a good source of antioxidants with the highest capacity found in the outer sections. Therefore, onion waste could be used to produce functional ingredients with important heath benefiting properties, due to the presence of bioactive compounds.

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Table 1. **Dry matter (g kg^{-1}) in whole onion and onion sections of cv. Recas**

	Brown skin	Top and Bottom	Outer scales	Inner scales	Whole onion
Dry matter	519± 18^{e}	132 ± 35^{d}	63 ± 3^{a}	69 ± 2^{b}	88 ± 7^{c}

Mean values followed by different superscript letter differ significantly when subjected to DMRT (P<0.005).

Table 2. Content of non-structural carbohydrates (mg g^{-1} DW) in whole onion and onion sections

	Sucrose	Glucose	Fructose	Total Fructans	NSC
Whole onion	**65 ± 3 ^{c}**	**199 ± 7 ^{b}**	**175 ± 5 ^{b}**	**53 ± 1 ^{c}**	**492 ^{c}**
% NSC	13	40	36	11	100
Inner scales	**65 ± 1 ^{c}**	**221 ± 4 ^{d}**	**202 ± 2 ^{d}**	**54 ± 2 ^{c}**	**542 ^{d}**
% NSC	12	41	37	10	100
Outer scales	**38 ± 1 ^{b}**	**210 ± 3 ^{c}**	**195 ± 3 ^{c}**	**26 ± 2 ^{b}**	**469 ^{b}**
% NSC	8	45	42	5	100
Top-bottom	**26 ± 1 ^{a}**	**39 ± 2 ^{a}**	**51 ± 4 ^{a}**	**8 ± 1 ^{a}**	**124 ^{a}**
% NSC	21	31	41	6	100

NSC = sucrose + glucose + fructose + total fructans

Mean values within a column followed by different superscript letter differ significantly when subjected to DMRT (P<0.005).

560 **Table 3. Content of fructooligosaccharides (mg g^{-1} DW) in whole onion and onion**

561 **sections**

	1-F-Nystose (GF_4)	Nystose (GF_3)	Kestose (GF_2)	Total FOS
Whole onion	**2.4 ± 0.6 [c]**	**17.5 ± 1.5 [c]**	**18.6 ± 0.4 [c]**	**38.5 [c]**
% total FOS	6	45	48	100
Inner scales	**2.3 ± 0.0 [c]**	**17.9 ± 0.1 [c]**	**19.2 ± 0.5 [c]**	**39.4 [c]**
% total FOS	6	45	49	100
Outer scales	**0.9 ± 0.0 [b]**	**9.6 ± 0.0 [b]**	**12.1 ± 0.6 [b]**	**22.6 [b]**
% total FOS	5	42	53	100
Top-bottom	**0.5 ± 0.0 [a]**	**1.2 ± 0.1 [a]**	**4.7 ± 0.1 [a]**	**6.4 [a]**
% total FOS	8	19	73	100

562 Mean values within a column followed by different superscript letter differ significantly when subjected

563 to DMRT (P<0.005).

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565 **Table 4. Content of total Sulphur and ACSOs in whole onion and onion sections**

	Total S (µmoles g^{-1} DW)	Total ACSOs (µmoles g^{-1} DW)	Total S-ACSOs vs. total S (%)	PECSO (mg g^{-1} DW)	MCSO (mg g^{-1} DW)	Total ACSOs (mg g^{-1} DW)
Whole onion	121.9 ± 3.2 ^{c}	23.8 ^{c}	19.5	2.2 ± 0.2 ^{b}	2.0 ± 0.1 ^{c}	4.2 ^{c}
Inner scales	153.1 ± 5.1 ^{e}	54.2 ^{e}	35.4	6.0 ± 0.5 ^{d}	3.1 ± 0.2 ^{d}	9.1 ^{e}
Outer scales	100.2 ± 2.1 ^{b}	29.9 ^{d}	29.9	3.6 ± 0.1 ^{c}	1.4 ± 0.1 ^{b}	5.0 ^{d}
Top-bottom	143.8 ± 3.3 ^{d}	22.2 ^{b}	15.5	2.4 ± 0.1 ^{b}	1.3 ± 0.1 ^{b}	3.7 ^{b}
Brown Skin	15.6 ± 0.6 ^{a}	4.6 ^{a}	29.6	0.4 ± 0.0^{a}	0.3 ± 0.0 ^{a}	0.7^{a}

566 Mean values within a column followed by different superscript letter differ significantly when subjected to DMRT (P<0.005).

Table 5. Content of total phenols, flavonoids and flavonols, and antioxidant capacity in whole onion and onion sections

	Total Phenols (mg GAE g^{-1}DW)	Total Flavonoids (mg QE. g^{-1} DW)	Total Flavonols (mg g^{-1} DW)	Antioxidant activity (µmoles Fe^{2+} g^{-1} DW)
Whole onion	17.3 ±1.3 [b]	10.3 ± 0.3 [b]	9.0 ± 1.4 [c]	83.5 ± 1.8 [b]
Inner scales	9.4 ± 0.6 [a]	7.0 ± 0.1 [a]	6.1 ± 0.2 [a]	28.7 ± 1.7 [a]
Outer scales	19.7 ± 1.6 [b]	19.5 ± 0.7 [c]	19.2 ± 1.4 [e]	105.1± 0.6 [c]
Top-Bottom	30.5 ± 2.0 [c]	25.9 ± 0.7 [d]	15.3 ± 1.4 [d]	156.1± 1.6 [d]
Brown skin	52.7 ± 0.9 [d]	43.1 ± 1.8 [e]	7.9 ± 0.4 [b]	227.8 ± 3.2 [e]

Mean values within a column followed by different superscript letter differ significantly when subjected to DMRT (P<0.005).

576 **Table 6. Content of quercetin and their glucosides (mg g^{-1} DW) in whole onion and onion sections**

	Quercetin	Quercetin 3'-glucoside	Quercetin 4'-glucoside	Quercetin 3,4'-diglucoside	Isorhamnetin 3, 4'-diglucoside	Isorhamnetin 4'- glucoside	Ratio Di:Mon[1]
Whole onion	0.91 ± 0.04 [c]	0.16 ± 0.03 [b]	4.02 ± 0.53 [b]	3.1 ± 0.68 [b]	0.12 ± 0.02 [a]	0.53 ± 0.07 [c]	1:1.3
Inner scales	0.02 ± 0.00[a]	0.10 ± 0.00 [a]	2.00 ± 0.07 [a]	3.70 ± 0.11 [b]	0.12 ± 0.00 [a]	0.25 ± 0.00 [a]	1.8:1
Outer scales	0.59 ± 0.04 [b]	0.42 ± 0.03 [d]	7.37 ± 0.53 [d]	9.49 ± 0.68 [d]	0.37 ± 0.02 [c]	1.03 ± 0.07 [e]	1.3:1
Top-Bottom	1.21 ± 0.09 [d]	0.40 ± 0.03 [d]	6.35 ± 0.60 [c]	5.90 ± 0.50 [c]	0.57 ± 0.04 [d]	0.86 ± 0.07 [d]	1:1.1
Brown skin	1.61 ± 0.02 [e]	0.31 ± 0.01 [c]	5.16 ± 0.34 [c]	0.30 ± 0.03 [a]	0.19 ± 0.01 [b]	0.32 ± 0.02 [b]	1:17

577 Mean values within a column followed by different superscript letter differ significantly when subjected to DMRT (P<0.005)

578 [1]Ratio Di:Mon, quercetin 3,4'-diglucoside:quercetin 4'-glucoside

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