Pectin content and composition from different food waste streams

Judith Müller-Maatsch, Mariangela Bencivenni, Augusta Caligiani, Tullia Tedeschi, Geert Bruggeman, Montse Bosch, Janos Petrusan, Bart Van Droogenbroeck, Kathy Elst, Stefano Sforza

PII: S0308-8146(16)30012-7
DOI: http://dx.doi.org/10.1016/j.foodchem.2016.01.012
Reference: FOCH 18586

To appear in: *Food Chemistry*

Received Date: 30 June 2015
Revised Date: 11 November 2015
Accepted Date: 5 January 2016

Please cite this article as: Müller-Maatsch, J., Bencivenni, M., Caligiani, A., Tedeschi, T., Bruggeman, G., Bosch, M., Petrusan, J., Van Droogenbroeck, B., Elst, K., Sforza, S., Pectin content and composition from different food waste streams, *Food Chemistry* (2016), doi: http://dx.doi.org/10.1016/j.foodchem.2016.01.012

Pectin content and composition from different food waste streams

Judith Müller-Maatsch[a], Mariangela Bencivenni[a], Augusta Caligiani[a], Tullia Tedeschi[a], Geert Bruggeman[b], Montse Bosch[c], Janos Petrusan[d], Bart Van Droogenbroeck[e], Kathy Elst[f], Stefano Sforza[a]

a) Department of Food Science, University of Parma, Parma, Italy

b) Nutrition Sciences N.V., Drongen, Belgium

c) Leitat Technological Center, Terrassa, Barcelona, Spain

d) IGV GmbH, Nuthetal, Germany

e) Institute for Agriculture and Fisheries Research, Merelbeke, Belgium

f) Flemish Institute for Technological Research, Mol, Belgium

In memory of Anna Surribas, scientist and friend

Corresponding author:

Stefano Sforza, PhD

Department of Food Science

Parco Area delle Scienze 17a, University Campus

University of Parma

I-43124 – Parma

Italy

Tel. +39-0521-905406

e-mail: stefano.sforza@unipr.it

ABSTRACT

In the present paper, 26 food waste streams were selected according to their exploitation potential and investigated in terms of pectin content. The isolated pectin, subdivided into calcium bound and alkaline extractable pectin, was fully characterized in terms of uronic acid and other sugar composition, methylation and acetylation degree. It was shown that many waste streams can be a valuable source of pectin, but also that pectin structures present a huge structural diversity, resulting in a broad range of pectin structures. These can have different physicochemical and biological properties, which are useful in a wide range of applications. Even if the data could not cover all the possible batch by batch and country variabilities, to date this represents the most complete pectin characterization from food waste streams ever reported in the literature with a homogeneous methodology.

Keywords: pectin, food waste, uronic acid, methylation degree, acetylation degree

1. Introduction

Pectins are polysaccharides occurring ubiquitously in plants. They are present in the cell walls located in the middle lamella, and primary and secondary cell wall. The chemical structure of pectin is heterogeneous, depending on the origin, location in the plant and extraction method. The main structural motif is made by uronic acid residues linked through α-1-4-glycosidic bonds, according to the definitions by the Joint FAO/WHO Expert Committee on Food Additives and the European Commission, pectin needs to contain at least 65% of galacturonic acid. Beyond the standard structural feature of the galacturonyl polymer, the homogalacturonan, different pectic structures have been described in literature. In rhamnogalacturonan I, the galacturonic acid residues are partly substituted by α-1-2 linked rhamnose residues. In addition several side chains containing sugars, such as xylose, arabinose, glucose, fucose, mannose or galactose, have been found to be linked to the main backbone structure. Moreover, the galacturonic acid moieties in the backbone can also be esterified on the carboxylic acid moiety by methyl groups, whereas in their O2/O3 positions, esters can be also present by linkage with the acetyl group or, less commonly, with the feruloyl group. (Levigne, Thomas, Ralet, Quemener & Thibault, 2002; Müller-Maatsch, Caligiani, Tedeschi, Elst & Sforza, 2014)

Pectins are widely used as technological adjuvants in the food industry, fully exploiting their structural diversity. Different structures lead to different gelling properties, emulsion activities, emulsion stabilities and release effects in complex food matrices. Pectin can also be used not only to produce jellies or fillings for bakery, but also in beverages made of milk, soy or wheat and in food and pharmaceutical preparations as functional ingredients for release control of oligomers showing prebiotic activities. (Babbar, Dejonghe, Gatti, Sforza & Elst, 2015) Due to the rising global demand in pectin, the identification of different sources is of great interest (Willats, Knox & Mikkelsen, 2006; Babbar et al., 2015).

Among the possible sources of pectic polysaccharides, food waste streams are of major interest. As a matter of fact, the exploitation of waste streams by the agrifood industry has been an increasingly important issue over several years. Large volumes of waste have been used as animal feed, fertilizers or for the generation of bio-energy, but recently extraction of more valuable components in the residues is the subject of many research projects (Pfaltzgraff, Bruyn, Cooper, Budarin & Clark, 2013). These high-value compounds can be classified as insoluble (fibers), water-soluble or lipid soluble compounds (Schieber, Stintzing & Carle, 2001). Innovative products coming from waste streams can therefore include dietary fibers with different technological and nutritional properties as well as food additives (e.g. bioflavours) and bioadsorbents (e.g. wastewater treatment) (Laufenberg, Kunz & Nystroem, 2003). In this line of research, several food wastes, such as apple, citrus, sugar beet, pea and cauliflower, have been investigated in order to isolate pectin. (McKnee & Latner, 2000). However, a detailed characterization of the amount and the structure of the pectin in different waste streams, which is essential in order to assess their potential techno- and biofunctionality, is still largely incomplete.

In the present paper, 26 food waste streams selected according to their exploitation potential (mainly due to their potential nutritional properties, quantities produces and seasonality) in the framework of the EU project NOSHAN (EU Grant Agreement n° 312140), have been investigated in terms of pectin content, fully characterizing the isolated pectin in terms of uronic acid and other sugar composition, methylation and acetylation degree. Even if the data could not cover all the possible batch by batch and country variabilities, it is shown that many waste streams can be a valuable source of pectin. Pectin structures also present a huge structural diversity, resulting in a broad range of pectin structures, which can have different physicochemical and biological properties that are useful in a wide range of applications.

To date, this represents the most complete pectin characterization from food waste streams ever reported in the literature.

2. Materials and Methods

2.1. Materials

The following samples coming from industrial processing plants all around Europe were considered: sugar beet flakes, apple pomace, pumpkin without kernels, pea pod, cabbage fresh and sour, sour cucumber, onion hull, apple cake, seabuckthorn pulp, seabuckthorn seed (press cake), pumpkin kernel cake, parsley, hop, rapeseed press cake, sabal (provided by IGV GmbH, Germany, through collection at local plants), olive pomace, orange peels, grape pomace (provided by Leitat Technological center, Spain, through collection at local plants), tomato skins (provided by University of Parma, Italy, through collection at local plants), berries (provided by Flemish Institute of Technological Research, Belgium, through collection at local plants), whole apples, whole pears, belgian endive root and leaves, leek (provided by the Institute for Agriculture and Fisheries Research, Belgium, through collection at local plants).

2.2. Dry matter determination

About 5 g of sample were weighed and dried for 4 h in an oven preheated to 103°C. After cooling for 30 minutes they were weighed again and this value was taken as the dry matter content.

2.3. Cell Wall Isolation

Isolation of the cell wall was performed adapting the method by Melton & Smith (2001). Twenty-five gram of sample was ground to a powder, mixed with 100 ml 80% phenol- 0.5 M HEPES buffer (w/v) and homogenized with an Ultraturrax T-50 basic (IKA-Werke, Staufen im Breisgau, Germany, 2-3 min, 4,000 rpm). The mixture was separated in a centrifuge, model 5804 (Eppendorf AG, Hamburg, Germany) by centrifuging for 20 min at 3220 x g at room temperature in HDPE centrifuge bottles, and the supernatant removed. The separation of the soluble cell matrix contents was done using 50 mM HEPES buffer (pH 6.7). The pellet was treated (incubation 6 and 24 hr) with DMSO 90% (v/v) and furthermore incubated 1h at

40°C with 200 U porcine pancreatic α-amylase stabilized by 20 mM HEPES buffer with 20 mM $CaCl_2$ (pH 6.9), to remove starch from the samples. The pellet was washed with 20 mM HEPES buffer with 20 mM $CaCl_2$ (pH 6.9) and the supernatant removed.

2.4. Sequential Extraction

The isolation method followed instructions by Melton et al. (2001). Cell walls of 25 g plant tissue were treated twice (6 and 12 hr) with 50 mM trans-1,2-diaminocyclohexane-N,N,N,N-tetraacetic acid (CDTA) in 50 mM potassium acetate buffer (pH 6.5), to extract the chelating agent soluble solids (CASS). The supernatant was separated in a centrifuge model 5804 (Eppendorf AG, Hamburg, Germany) by centrifuging for 20 min at 3220 x g at room temperature in HDPE centrifuge bottles and dialyzed with 0.1 M ammonium acetate buffer (pH 6.5, 1 day, 3 changes, 4°C) followed by H_2O (3 days, 3 changes at 4°C). The solution was freeze-dried (LIO 5P, VWR International PBI Milano, Italy) and the residue was weighted to determine the yield of CASS related to the dry matter content of the food waste streams.

The pellet was treated with 50 mM Na_2CO_3/ 20 mM $NaBH_4$ twice (16 and 2 hr) at 4°C to extract the dilute alkaline soluble solids (DASS). The supernatant was separated in a centrifuge model 5804 (Eppendorf AG, Hamburg, Germany) by centrifuging for 20 min at 3220 x g at room temperature in HDPE centrifuge bottles and neutralized using acetic acid and dialyzed with H_2O (3 days, 3 changes, 4°C). The solution was freeze-dried (LIO 5P, VWR International PBI Milano, Italy) and the residue was weighted to determine the yield of DASS related to the dry matter content of the food waste streams.

The total pectin yield was taken as the combined weights of the freeze-dried CASS and DASS related to the dry matter content of the food waste streams.

2.5. Uronic acid content

Sample preparation and measurement followed instructions by Melton & Smith (2001) with galacturonic acid as a standard. 10 mg of freeze-dried pectin samples were hydrolyzed by adding 2 ml of concentrated sulfuric acid for 10 minutes, under constant stirring and cooling

in an ice bath. Then 0.5 ml of bidistilled water was added, the mixture was stirred and further diluted with a further 5 ml of bidistilled water. The samples were was separated in a centrifuge model 5804 (Eppendorf AG, Hamburg, Germany) by centrifuging for 20 min at 3220 x g at room temperature in HDPE centrifuge bottles and the supernatant was used for the colorimetric assay as follows. To 400 µl of supernatant or standard (galacturonic acid in water at different concentrations ranging from 25 µg/ 400µl until 300 µg/ 400µl), 40 µl of 4 M sulfamic acid/potassium sulfamate solution (pH 1.6) and 2.4 ml 75 mM sodium tetraborate/sulfuric acid solution were added. The mixture was heated (100°C) for 20 min and then cooled. To the sample control, 80 µl 0.5% NaOH were added to determine the sugar colouring. To the sample and standard, 80 µl 255 M m-hydroxydiphenyl in 0.5% NaOH was added and the absorbance was measured after 10 minutes at 525 nm against a water blank in a UV/VIS LAMBDA BIO 20 spectrophotometer (Perkin Elmer, Waltham, MA, USA).

2.6. Degree of methylation and acetylation.

The method previously published by Müller-Maatsch et al. (2014) was followed. 30 mg of freeze-dried pectin samples were combined with 1 ml 0.4 M NaOH and stirred for 2 hours at room temperature in capped tubes. Afterwards the supernatant was separated in a centrifuge model 5804 (Eppendorf AG, Hamburg, Germany) by centrifuging for 20 min at 3220 x g at room temperature in HDPE centrifuge bottles, followed by the addition of 100 µl of internal standard solution (10 mg 3-(trimethylsilyl)propionate-d4 (TSP) in 5 ml D_2O) used to quantify the methanol and the acetic acid. The supernatant was filtered using a syringe equipped with 0.4 µm nylon filter and transferred in NMR-tubes. 1H NMR spectra were acquired on a VARIAN-INOVA 600 MHz spectrometer, equipped with a triple resonance inverse probe (HCN), operating at 599.736 MHz for proton. Spectra were acquired at 298 K, with 32K complex points, using a 90◦ pulse length. 128 scans were acquired with a spectral width of 7196.8 Hz, an acquisition time of 2.53 and a relaxation delay (d1) of 5 s. The experiments were carried out with water suppression by low power selective water signal presaturation

during 5 s of the relaxation delay. The NMR spectra were processed by MestreC software. The spectra were Fourier transformed with FT size of 64K and 0.2 Hz line-broadening factor, phased and baseline corrected, and referenced to 3-(trimethylsilyl)-propionate-d4 (TSP) peak (0 ppm). The quantitative determination of acetic acid and methanol was obtained by manual integration of the corresponding signals (1.92 ppm for acetic acid, 3.36 for methanol) and the comparison with TSP area. The values obtained by the integration were converted in mass value (mg) according to the formula reported in Müller-Maatsch et al. (2014). The accuracy of the quantitative data was assured by the relaxation delay, determined by T1 measurements, which was set in order to allow the complete relaxation of the nuclei.

2.7. Neutral sugars

Pectin samples were hydrolysed following the method previously published by Melton et al. (2001). 10 mg of pectin sample were hydrolyzed with 3 ml 2 M triflouracetic acid under nitrogen for 60 min at 121°C. To the hydrolysed mixture, 1 ml phenyl-β-D-glucopyranoside (500 ppm) was added as internal standard. The samples were clarified by syringe filtration on nylon filters (40 µm) and the filtrate evaporated to dryness with nitrogen. With 1800 µl N-N-dimethylformamide and 200 µl N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) with trimethylchlorosilane (TMCS) the sugars were silylated for 60 min at 60°C. The GC/MS analysis was carried out with a Agilent Technology 6890N Network GC System equipped with a 5973 MS Detector, using a capillary column HP-5MS 0,25 mm x 30 m x 0,25 µm, injection volume of 1 µl, initial temperature 60°C, split injection (ratio 20:1), carrier gas helium, following this temperature ramp: 10°C/min until 160°C, then 10°C/min until 220°C, then 20°C/min until 270°C.

2.8. Statistical analysis

All measurements were done in duplicate and the average values with the corresponding standard deviations were calculated.

3. Results

The pectin content was determined for the two fractions of pectin, the one soluble in chelating agents (calcium-bound pectin) and the other one soluble in alkaline solution (ester linkage-bound pectin). According to the method applied here, chelating agent solutions first extract soluble pectic polysaccharides (Melton et al., 2001) yielding, after freeze drying, the chelating agent soluble solid (CASS, details in the experimental section). CDTA actually solubilises pectic polysaccharides supposedly by disrupting the ionic bridges between calcium and non-esterified galacturonic residues. Chelating agents enhance the extractability of the pectic polysaccharides in mild conditions and reduce the degradation and production of artefacts. This was the main reason for choosing this method, even if quite cumbersome, exactly because it is known to yield pectins with their native structure as intact as possible (Renard & Thibault, 1993) even if co-extraction of proteins (14-44% w/w according to Pustjens, Schols, Kabel & Gruppen, 2013) or other polysaccharides as hemicelluloses (Mateos-Aparicio, Redondo-Cuenca & Villanueva-Suárez, 2010) can lead to aberrant estimations of the pectin content. This method might also lead to incomplete recovery of the ester-bound pectin fraction. Thus, in order to obtain the ester-bound pectin, an alkaline extraction with 50 mM Na_2CO_3/20 mM $NaBH_4$ was then also performed on the residual from the extraction with CDTA yielding, after freeze drying, the diluted alkaline soluble solid (DASS, details in the experimental section). The DASS fraction contains the previous ester-bound pectin as well as traces of hemicelluloses. $NaBH_4$ was added to alkaline solutions to reduce the reducing end of the polysaccharides and therefore prevent base peeling of polysaccharides (Melton et al., 2001).

The total pectin content, also divided in the CASS and DASS fractions, is shown in Figure 1 for the different food wastes, expressed in mg/g sample (as dry matter), in decreasing order of content. The highest levels of CASS were obtained from orange peel (126 mg/g), pumpkin (85 mg/g) and parsley (47 mg/g), whereas the highest values of DASS came from pumpkin

(150 mg/g), orange peels (121 mg/g), and endive roots (119 mg/g). As displayed in Figure 1, the DASS pectin fraction was almost always the more consistent one (the lower bound represented by leek leaves, with a CASS/DASS ratio of 0.21). Nevertheless, in few samples the CASS fraction was more abundant (olive pomace CASS/DASS ratio 1.27, grape pomace 1.45, tomato skins 3.24).

Although the results can not be considered representative of all the possible variations present in food waste streams in Europe, the homogeneous analytical methodology applied showed the impact of the processing technology on pectin yield and composition, as indicated by the differences between apple pomace (CASS 14 mg/g DM, DASS 41 mg/g DM) and apple cake (CASS 13 mg/g; DASS 73 mg/g). Also the different plant tissues with different pectin content obviously affected the yield: whole apple, less rich in skins, had a lower amount of pectin per gram of dry matter than the previously reported apple pomace and apple cake (CASS 10 mg/g DM, DASS 10 mg/g DM). Endive leaves (CASS 18 mg/g DM, DASS 85 mg/g DM) and endive roots (CASS 29 mg/g DM, DASS 102 mg/g DM) also showed a different pectin contents.

The uronic acid content in the obtained polysaccharides is a good indication of the quality of the pectin in the extract. The amount of uronic acids in our samples was determined spectrophotometrically by using m-hydroxydiphenyl as a colouring agent, which is the common way to determine uronic acids in the literature (Melton et al., 2001). The results are reported in Figures 2 (uronic acid content in CASS samples) and 3 (uronic acid content in DASS samples), expressed as mg of uronic acid for g of extracted pectin fraction. Samples are reported in the same order as Figure 1, according to the decreasing content of total pectin. The amount of uronic acids in the extract can vary due to the presence of neutral sugars replacing galacturonic acids. Furthermore, the quality of the data can be affected by overestimation of uronic acid in some samples due to the interference in the spectrophotometrical measurement of extracted co-products, which might lead to 10-20% overestimation of the actual content of

uronic acid. Taking into account these limitations of the applied method and the expected errors, the trends in galacturonic acid content were anyway very clear. Highest results in uronic acid content, and therefore mostly homogalacturonan, was extracted with chelating agents solution from onion hull (1146 mg/g CASS), orange peel (1099 mg/g CASS), leek (890 mg/g CASS), endive (993-1033 mg/g CASS), seabuckthorn pulp (1002 mg/g CASS) and fresh cabbage (934 mg/g CASS). Solids extracted in diluted alkaline solutions were found to have highest yields in uronic acid in the case of apple pomace (1066 mg/g DASS), hop (974 mg/g DASS), seabuckthorn pulp (968 mg/g DASS), onion (958 mg/g DASS) and pea pod (949 mg/g DASS).

In order to determine the neutral sugar contents, pectic polysaccharides extracted by chelating agents were then hydrolyzed using TFA, releasing the neutral sugars, even if a full hydrolysis of the polysaccharides was unlikely (Melton et al., 2001). Silylation of neutral sugars and other compounds was then performed, in order to make them amenable for GC-MS detection, as previously reported (Reinders & Thier, 1999; Caligiani, Malavasi, Palla, Marseglia, Tognolini & Bruni, 2013),. The results of the total amount of sugars occurring and the detailed composition are reported in Table 1. The concentration of neutral sugars of pectic polysaccharides again was found to be variable among the different samples, according to the different waste streams, the CASS and DASS fraction, the treatment of samples with same origins during food processing as well as different parts of one plant. Highest neutral sugar content in CASS extracts was found in sugar beet (386 mg/g CASS), pea pod (310 mg/g CASS) and olive pomace (305 mg/g CASS). Values for neutral sugar obtained in DASS reached 442 mg/g DASS in fresh cabbage, 422 mg/g DASS in orange peels and 373 mg/g DASS in olive pomace. Not surprisingly, samples with the lowest amount of uronic acid also had the highest amount of neutral sugars.

The methylation and the acetylation degree was done after alkaline saponification (Levigne et al., 2002) by determining methanol and acetic acid by NMR after performing the

saponification directly in alkaline deuterium oxide (Müller-Maatsch et al., 2014). The esterification degree is shown only for CASS (figure 4), as the extraction with diluted alkaline used for DASS causes the hydrolysis of the ester groups, thus making the esterification degree completely unreliable. Highest values in methylation degree were obtained in apple (whole apple 57%), even if after industrial processing this valued decreased (apple cake 36-40%), as well as in berries (42%), seabuckthorn (32%) and pear (30%). The acetylation degree has not been reported frequently on all samples analysed for pectic polysaccharides, also on account of the fact that it is lower than the methylation degree. Actually, the highest values were determined in sugar beet flakes (18%), rapeseed press cake (13 %) and pea pod (10%).

4. Discussion

4.1. General.The main aim of this study was to investigate the by-products of plant processing food industry for the potential content of valuable pectic polysaccharides. The data here presented, covering 26 different food wastes, cannot be considered a complete and exhaustive description of all the possible batch by batch variations in every waste stream analysed, nor covering for all the possible variations among different countries. Anyway, due to the homogeneous methodological approach applied, the analysed samples can be considered a meaningful survey of the waste streams considered, since the batches collected were the average mixtures generated at different stages of agri-food chain manufacturing sites, which process raw materials from different countries of Europe. The data obtained on the pectin content of the various food waste streams are discussed below, compared with the data reported in the literature (when available) on the corresponding content in the original food material.

4.2. Orange Peel

The highest yield of pectic polysaccharides was obtained in orange peel with 247 mg/g sample on dry matter basis. This is already a common source for pectins, which are usually extracted with acidic extractants. Different technologies were also evaluated reaching 154.7 mg/g (traditional heating), 181.3 mg/g (microwave) and 204.4 mg/g (Ultra high pressure) of pectin in orange peels (Guo, et al., 2012). The CASS sugar composition consisted, beside uronic acid (of which 25% methylated), of arabinose (136 mg/g CASS) as the most abundant neutral sugar. DASS had instead more arabinose (266 mg/g DASS) and galactose (105 mg/g DASS), in agreement with a recent report (Chau & Huang, 2003). The high content of pectic polysaccharides and their composition indicate this waste stream as an ideal source of dietary fibre for nutritional factors (Chau et al., 2003) or as texturizer or stabilizer due to its gelling

property and rheological behaviour in a variety of food, pharmaceutical and cosmetic products (Guo, et al., 2012).

4.3. Pumpkin and pumpkin kernel cake

In the literature, pumpkin polysaccharides from styrian oil-pumpkin pulp extracted at pH 4 with the chelating agent EDTA yielded 24 mg/g of pectic material (Košťálová, Hromádková & Ebringerová, 2013). Higher yields were obtained though by combining an acid extraction (42 mg/g) with a microwave treatment determining 113 mg/g pectic polysaccharides in squash pumpkin pulp (Yoo, et al., 2012). The sum of pectic polysaccharides determined in this study were 235 mg/g sample dry matter, which is higher than previously reported, due to the fact that the whole pumpkin (pulp and peel) was used as sample material. Only small amounts of neutral sugars were found: arabinose (3.2 % of CASS) and xylose (2.6% of CASS) had the highest values. The uronic acid extracted with a chelating agent solution (445 mg/g CASS; 536 mg/g DASS) was only partly esterified (18% methylation degree and 3% acetylation degree). The composition was reported in the literature as being 543 mg/g uronic acid, with a methylation degree of 28% in the extracts and a large amount of phenolic compounds, proteins and neutral sugars (Košťálová, Hromádková & Ebringerová, 2013). Due to its behaviour in forming viscose solutions and surface tensions, similar to citrus peels, it can be used as food additive (Fissore, Rojas, Gerschenson & Williams, 2013). Furthermore the extracts are suggested to have a positive effect on gut bacteria (Jun, Lee, Song & Kim, 2006). Pumpkin kernel cake, on the other side, is a by-product of processing industry exploiting the valuable pumpkin seed oil. The extraction of pectic polysaccharides led to very low yields (29 mg CASS/g; 30 mg DASS/g) and with low uronic acid content indicating a large co-extraction of proteins, thus very little and low quality pectic material.

4.4. Leek

Pectic polysaccharides of leek were extracted mainly by alkaline solutions (25 mg CASS/g; 119 mg DASS/g). Results of uronic acid and neutral sugars indicate a high amount of

methylated uronic polysaccharides (DE 26%, DA 3%) with less side chains containing neutral sugars, mainly galactose. These results agree with the previously reported ones, which proposed that the presence of side chains containing galactose have a positive effect on the biological activity of these pectic polysaccharides (Kratchanova, Nikolova, Pavlova, Yanakieva & Kussovski, 2010).

4.5. Belgian endive leaves and roots

The extraction with chelating agents (roots 29 mg/g; leaves 19 mg/g) resulted in both samples in lower yields than the alkaline one (roots 102 mg/g; Leaves 85 mg/g), indicating a higher content of bound pectin. The detection of uronic acid was very high in leaves, both CASS and DASS, as well as in roots CASS. Findings here are indicating a large amount of pectin, with a high methylation degree, particularly in roots (DE Roots 23% Leaves 12%; DA Roots 3%, Leaves 2%), with arabinose as the main neutral sugar. This composition strictly resembles sugar beet pectin. In the literature, the distribution of neutral sugars of endive pulp pectin extracted using enzymes led to different results. Though arabinose was also determined to be the main neutral sugar, higher values were obtained in the neutral sugars mannose, galactose and glucose. The value of galacturonic acid was less than that obtained with extraction by chemicals (Zykwinska, Boiffard, Kontkanen, Buchert, Thibault & Bonnin, 2008). The higher yields of pectin in roots than in leaves was also suggested previously (Villanueva-Suárez, Redondo-Cuenca, Rodríguez-Sevilla & de las Heras Martínez, M., 2003).

4.6. Fresh and sour Cabbage

The yield of pectic polysaccharides in fresh and fermented cabbage differed little when extracted with chelating agent solutions (Fresh 30 mg CASS/g; Sour 23 mg CASS/g) and more in alkaline solutions (Fresh 93 mg DASS/g; Sour 44 mg DASS/g). A similar effect in loss of dietary fibre was mentioned for cabbage while boiling and storing (Wennberg, Engqvist & Nyman, 2003). The composition of pectic polysaccharides in fresh and sour cabbage ranged from homogalacturonans in CASS (uronic acid content 934 mg/g CASS) to

galacturonans with a high amount of side chains containing arabinose and galactose in DASS. Galactose and arabinose rich pectic polysaccharides have been reported previously in fresh cabbage and are studied for their immunological activity (Westereng, Michaelsen, Samuelsen & Knutsen, 2008). The methylation (Fresh 19%, sour 12%) and acetylation degree (fresh 5%, sour 4%) indicate that this pectic material might have good gelling properties, which have not been reported yet.

4.7. Onion

Pectic substances extracted from onion hulls were composed mainly of uronic acids with a methylation degree of 19% and acetylation degree of 2%, indicative for highly polymerized polygalacturonates. These findings are in line with what has been previously reported in the literature, where also very efficient immunostimulating effects as well as physical properties were observed (Patra, et al., 2013).

4.8. Parsley

There has not been any research done on parsley pectin, so the values obtained in this paper of 47 mg/g in CASS and 67 mg/g DASS are the first reported ones. The extract had a uronic acid content between 867 mg/g CASS and 858 mg/g DASS, indicating a high purity of pectin. The neutral sugars detected were mainly arabinose (6.51% CASS; 10.75% DASS) and galactose (6.45% CASS; 13.06 % DASS). The low degree of methylation and acetylation indicates physical properties similar to pumpkin or sugar beet pectic polysaccharides. Due to the high amount of neutral sugars it could be used as functional food ingredient.

4.9. Apple, apple cake and apple pomace

By-products of apple processing industry are after citrus fruits the second most used source of pectin (May, 1990). Three samples of apple origin were investigated in this paper. Whole apples, discarded from fresh consumption, apple cake and apple pomace from the fruit processing industry. Yields were higher in the processed products: apple 10 mg CASS /g, 10 mg DASS /g; apple cake 13 mg CASS/g, 74 mg/g DASS; apple pomace 14 mg CASS/g, 42

mg DASS/g. Uronic acid content of the extracted pectic polysaccharides was in all three samples lower in the extraction with chelating agent (apple 488 mg/g CASS, apple cake 408 mg/g CASS, apple pomace 781 mg/g CASS) than in the diluted alkaline extraction (apple 656 mg/g DASS, apple cake 802 mg/g DASS, apple pomace 1067 mg/g DASS). CASS as well as DASS were rich in neutral sugars arabinose 6-9%, galactose 2-4%, rhamnose 1-4%, glucose 1-7% and xylose 1-5%. Traces of mannose and fucose were found as reported earlier (Renard et al., 1993). The CASS fraction contained highly methylated galacturonans, but with a wide range (26-60%). This data supports the decrease of methylation during juice production, likely due to the activity of pectin-methylesterase.

4.10 Pea

Extraction of pea pods yielded 10 mg CASS/g and 73 mg DASS/g, values which are in agreement with the total yield of pectic polysaccharides in literature (Mateos-Aparicio, Redondo-Cuenca & Villanueva-Suárez, 2012). The pectic polysaccharide fractions were rich in uronic acid (70-95%), highly methylated (30%) and acetylated (10%), and rich in arabinose, xylose and galactose as mentioned previously (Wheightman, Renard, Thibault, 1995). There has not been any study yet reported on the technological application of pea hull pectin, despite the purity and high methylation degree.

4.11. Cucumber

Pectic polysaccharides of cucumber (sour) were 27 mg CASS/g and 38 mg DASS/g. The CASS extract contained more homogalacturonans indicated by the high uronic content and small amounts of neutral sugar, mainly galactose and fucose. In contrast, the uronic acid content was lower in DASS with a high amount of neutral sugar (galactose, arabinose and fucose). Galacturonic residues were methylated at 25 % and partially acetylated 4%. As reported by McFeeters et al., the fermentation of cucumber led to a loss in esterification from 54% in fresh cucumber to 16% in fermented one (McFeeters & Armstrong, 1984).

4.12. Sugar beet

Yields of pectic polysaccharides obtained from sugar beet pulp were 28 mg CASS/g and 32 mg DASS/g. These results are lower than previously reported, which can be explained by the different method used for the extraction (Oosterveld, Beldman, Schols & Voragen, A. G. J., 1996). The composition of the fractions were in agreement with the literature (Yapo, Robert, Etienne, Wathelet & Paquot, 2007): uronic acid content ranged between 653 mg/g CASS and 689 mg/g DASS and high values of arabinose and small amounts of galactose and rhamnose were detected. This indicates the occurrence of rhamnogalacturonan, arabinan and homogalacturonan in both extracts. The galacturonic residues in sugar beet are known to be both methylated (29%) and acetylated (18%) (Renard et al., 1993).

4.13. Berries

The by-product of berry juice production contained 25 mg CASS/g and 33 mg DASS/g which is in agreement with the yields reported from bilberry and black currant press cake (Hilz, Bakx, Schols & Voragen, 2005). CASS was composed by 744 mg/g uronic acid with 42 % methylation degree and 1 % acetylation degree, arabinose, galactose and rhamnose. In DASS less uronic acid 596 mg/g and more neutral sugars were detected. Similar results were measured by Hilz et al. (2005), though the methylation degree and acetylation degree was different. Again, this might be explained by different sample pretreatment.

4.14. Rapeseed

Extraction yields of pectic polysaccharides were low in rapeseed press cake (25 mg CASS/g; 23 mg DASS/g). In accordance with the literature, the uronic acid content ranged from 85 mg/g CASS to 102 mg/g DASS with high levels of arabinose and xylose (Eriksson, Anderson & Aman, 1997). In CASS 25% of uronic acid was methylated and 13% esterified with acetic acid groups. The possibility of having proteins coextracted with the pectin fraction was mentioned previously in rapeseed meal (Pustjens et al., 2013).

4.15. Seabuckthorn pulp and see

448 The pulp of seabuckthorn was found to have more pectic polysaccharides (14 mg CASS/g
449 and 25 mg DASS/g), compared to the by-product seabuckthorn seeds (6 mg CASS/g, 8 mg
450 DASS/g). No further analysis was applied on the seed waste, given the very low amount of
451 pectin. Extracts of the pulp contained high amounts of uronic acid, halfway esterified and
452 partially acetylated, as well as arabinose and galactose in accordance with literature
453 (Dongowski, 1996).

454 4.16. Hop

455 The extraction of pectic material from hops yielded 9 mg CASS/g and 18 mg DASS/g.
456 Several neutral sugars were detected, with arabinose, galactose and xylose as the highest. The
457 uronic residues were partially methylated (14%) and acetylated (7%). Similar findings of
458 pectic extracts of hob using acidic solution were obtained previously (Oosterveld, Voragen,
459 A. G. J. & Schols, 2002).

460 4.17. Grape pomace

461 11 g CASS/g and 8 mg DASS/g pectic polysaccharides were extracted from grape pomace.
462 The larger amount was extracted by chelating agents as already reported for grape pomace of
463 different varieties (Deng, Penner & Zhao, 2011). A high uronic acid content was detected in
464 CASS (894 mg/ g CASS), low methylated (5%) with small amounts of arabinose and
465 galactose as reported for grape pulp (Saulnier & Thibault, 1987).

466 4.18. Olive pomace

467 Olive pomace, like grape pomace, has a low amount of pectic polysaccharides extractable by
468 chelating agents (14 mg CASS/g) or diluted alkaline solution (11 mg DASS/g). CASS
469 contains a high amount of uronic acid partially methylated and acetylated as well as high
470 amounts of neutral sugars, mostly arabinose and rhamnose. Similar findings were reported by
471 Jiménez et al. in untreated olive pulp (Jiménez, Rodríguez, Fernández-Caro, Guillén,
472 Fernández-Bolaños & Heredia, 2001).

473 4.19. Tomato

Pectic polysaccharides of CASS and DASS contained uronic acid (784 mg/g CASS and 330 mg/g DASS) with traces of neutral sugars, mostly galactose. The sugar composition in pectic polysaccharides is similar to the findings of Reinders et al. (1999). Galacturonic residues were halfway esterified and partially acetylated, albeit higher esterification up to 69% were reported previously (Seymour, Colquhoun, Dupont, Parsley & Selvendran, 1990). The differences can be explained again through the advanced ripening stage and the treatment of the starting material.

4.20. Pear

Pear pectic polysaccharides are similar to apple pectic polysaccharides though the yield of whole pears as starting material is much lower. A high amount of uronic acid and arabinose 6 % in CASS and 10 % in DASS, as well as traces of xylose and galactose were detected. The galacturonic residues were halfway esterified and partially acetylated. Renard et al. extracted from fresh pear cultivar "Gieser Wildeman", uronic acid rich fractions with a very low contents of neutral sugars, of which arabinose had the highest content (Renard, 2005). The similarity to apple pectin suggests the same physical properties.

4.21. Sabal

There was no literature found on the content of sabal pectic polysaccharides. So the data about this plant is the first time reported here. The amount of pectin was found to be very low, although the uronic acid content suggested a fair purity.

5. Conclusion

The investigation done here had the purpose to characterize the pectin composition of several waste streams of the plant processing industry. Although the data here reported do not exhaust all the possible variations possibly present in different batches and countries, this is the most complete survey of the of the pectic materials obtained from many diverse by-products with homogeneous methodology. It has shown that the pectin structures and yields present a very

high diversity according to the different origin. New insights in pectic polysaccharides distribution have been gained by performing the extraction with a chelating agent solution (CDTA) and a diluted alkaline solution, measuring in both fraction uronic acid and neutral sugars content, as well as degree of methylation and acetylation. This level of details in the molecular structures of pectin from by-products is unprecedented in the literature so far.

In general, the pectin structure of these waste streams seems to be well preserved compared to the original food material, with the notable exception of the methylation and acetylation degree, which are often lowered by the processing and/or by the action of the enzymes. The information about changes in pectic polysaccharide composition after processing is very valuable for the industry in view of a possible reutilization of these materials as a source of pectin. Even if the minimum amount of 65% uronic acids is usually required (thus preventing some of our material to be classified as truly pectin), however extracts that do not reach this limit might have interesting functionalites, and hence could be useful in different applications. The possible uses of pectic polysaccharides according to their composition, as food additive for their physical properties or as functional food for their bioavailability and bioactivity, can be derived from the data obtained in this study.

Acknowledgments

The research leading to these results has received funding from the European Union, Seventh Framework Program (FP7/2007- 2013), under Grant Agreement 312140 (Functional and Safe Feed from Food Waste – NOSHAN).

Captions to Tables and Figures

Figure 1. Calcium bound (dark bars) and ester linkage bound (light bars) pectin in the different food waste streams, expressed as mg/g of dry matter.

Figure 2. Uronic acid content in CASS (calcium-bound pectin), listed from left to right according to the total pectin content, expressed as mg/g of extracted pectin in the CASS fraction

Figure 3. Uronic acid content in DASS (dilute alkaline soluble pectin), listed from left to right according to the total pectin content, expressed as mg/g of extracted pectin in the DASS fraction

Figure 4. Degree of esterification (in percentage) in CASS (calcium-bound pectin), listed from left to right according to the total pectin content

Bibliography

Babbar, N., Dejonghe, W., Gatti, M., Sforza, S. & Elst, K. (2015). Pectic oligosaccharides from agricultural by-products: production, characterization and health benefits. *Critical Reviews in Biotechnology, 2,* 1–13.

Caligiani, A., Malavasi, G., Palla, G., Marseglia, A., Tognolini, M. & Bruni, R. (2013). A simple GC–MS method for the screening of betulinic, corosolic, maslinic, oleanolic and ursolic acid contents in commercial botanicals used as food supplement ingredients. *Food Chemistry, 136(*2), 735–741.

Chau, C.-F. & Huang, Y.-L. (2003). Comparison of the Chemical Composition and Physicochemical Properties of Different Fibers Prepared from the Peel of Citrus sinensis L. Cv. Liucheng. *Journal of Agricultural and Food Chemistry, 51(*9), 2615–2618.

Deng, Q., Penner, M. H. & Zhao, Y. (2011). Chemical composition of dietary fiber and polyphenols of five different varieties of wine grape pomace skins. *Food Research International, 44(*9), 2712–2720.

579 Dongowski, G. (1996). Investigation on polysaccharide, pectin and dietary fiber fractions of
580 buckthornton berries (Untersuchungen an Polysaccharid-, Pektin- und Ballaststoff-Fraktionen
581 von Sanddornbeeren). *Zeitschrift für Lebensmittel-Untersuchung und -Forschung, 203,* 302–
582 308.

583 Eriksson, I., Anderson, R. & Aman, P. (1997). Extraction of pectic substances from dehulled
584 rapeseed. *Carbohydrate Research, 301,* 177–185.

585 Fissore, E. N., Rojas, A. M., Gerschenson, L. N. & Williams, P. A. (2013). Butternut and
586 beetroot pectins: Characterization and functional properties. *Food Hydrocolloids, 31(*2), 172–
587 182.

588 Guo, X., Han, D., Xi, H., Rao, L., Liao, X., Hu, X., et al. (2012). Extraction of pectin from
589 navel orange peel assisted by ultra-high pressure, microwave or traditional heating: A
590 comparison. *Carbohydrate Polymers, 88(*2), 441–448.

591 Hilz, H., Bakx, E. J., Schols, H. A. & Voragen, A. G. (2005). Cell wall polysaccharides in
592 black currants and bilberries—characterisation in berries, juice, and press cake. *Carbohydrate*
593 *Polymers, 59(*4), 477–488.

594 Jiménez, A., Rodríguez, R., Fernández-Caro, I., Guillén, R., Fernández-Bolaños, J. &
595 Heredia, A. (2001). Olive Fruit Cell Wall: Degradation of Pectic Polysaccharides during
596 Ripening. *Journal of Agricultural and Food Chemistry, 49(*1), 409–415.

597 Jun, H.-I., Lee, C.-H., Song, G.-S. & Kim, Y.-S. (2006). Characterization of the pectic
598 polysaccharides from pumpkin peel. *LWT - Food Science and Technology, 39(*5), 554–561.

599 Košťálová, Z., Hromádková, Z. & Ebringerová, A. (2013). Structural diversity of pectins
600 isolated from the Styrian oil-pumpkin (*Cucurbita pepo* var. styriaca) fruit. *Carbohydrate*
601 *Polymers, 93(*1), 163–171.

602 Kratchanova, M., Nikolova, M., Pavlova, E., Yanakieva, I. & Kussovski, V. (2010).
603 Composition and properties of biologically active pectic polysaccharides from leek (Allium
604 porrum). *Journal of the Science of Food and Agriculture, 90,* 2046–2051.

605 Laufenberg, G., Kunz, B. & Nystroem, M. (2003). Transformation of vegetable waste into
606 value added products. *Bioresource Technology, 87(*2), 167–198.

607 Levigne, S., Thomas, M., Ralet, M.-C., Quemener, B. & Thibault, J.-F. (2002). Determination
608 of the degrees of methylation and acetylation of pectins using a C18 column and internal
609 standards. *Food Hydrocolloids, 16(*6), 547–550.

610 Mateos-Aparicio, I., Redondo-Cuenca, A. & Villanueva-Suárez, M. J. (2010). Isolation and
611 characterisation of cell wall polysaccharides from legume by-products: Okara (soymilk
612 residue), pea pod and broad bean pod. *Food Chemistry, 122(*1), 339–345.

613 Mateos-Aparicio, I., Redondo-Cuenca, A. & Villanueva-Suárez, M.-J. (2012). Broad bean and
614 pea by-products as sources of fibre-rich ingredients: potential antioxidant activity measured in
615 vitro. *Journal of the Science of Food and Agriculture, 92(*3), 697–703.

616 May, C. D. (1990). Industrial pectins: Sources, production and applications. *Carbohydrate*
617 *Polymers, 12(*1), 79–99.

618 McFeeters, R. & Armstrong, S. (1984). Measurement of Pectin Methylation in Plant Cell
619 Walls. *Analytical Biochemistry, 139,* 212–217.

620 McKnee, L. H. & Latner, T. A. (2000). Underutilized sources of dietary fiber: A review. *Plant*
621 *Foods for Human Nutrition, 55,* 285–304.

622 Melton & Smith (2001). Determination of Neutral Sugars by Gas Chromatography of their
623 Alditol Acetates. Determination of the Uronic Acid Content of Plant Cell Walls Using a
624 Colorimetric Assay. Isolation of Plant Cell Walls and Fractionation of Cell Wall
625 Polysaccharides. In Wrolstad, R. E.; Acree, T. E.; Decker, E. A.; Penner, M. H.; Reid, D. S.&
626 Schwartz, S. J., et al. (Eds.), Current Protocols in Food Analytical Chemistry (Unit E 3.2.1-
627 3.2.13). Hoboken, NJ, USA: John Wiley & Sons, Inc.

628 Müller-Maatsch, J., Caligiani, A., Tedeschi, T., Elst, K. & Sforza, S. (2014). Simple and
629 Validated Quantitative 1 H NMR Method for the Determination of Methylation, Acetylation,
630 and Feruloylation Degree of Pectin. *Journal of Agricultural and Food Chemistry, 62(*37),
631 9081–9087.

632 Oosterveld, A., Beldman, G., Schols, H. A. & Voragen, A. G. J. (1996). Arabinose and ferulic
633 acid rich pectic polysaccharides extracted from sugar beet pulp. *Carbohydrate Research, 288,*
634 143–153.

635 Oosterveld, A., Voragen, A. G. J. & Schols, H. A. (2002). Characterization of hop pectin
636 shows the presence of an arabinogalactan-protein. *Carbohydrate Polymers, 49,* 407–413.

637 Patra, P., Sen, I. K., Bhanja, S. K., Nandi, A. K., Samanta, S., Das, D., et al. (2013). Pectic
638 polysaccharide from immature onion stick (Allium cepa): Structural and immunological
639 investigation. *Carbohydrate Polymers, 92(*1), 345–352.

640 Pfaltzgraff, L. A., Bruyn, M. de, Cooper, E. C., Budarin, V. & Clark, J. H. (2013). Food waste
641 biomass: a resource for high-value chemicals. *Green Chemistry, 15(*2), 307.

642 Pustjens, A. M., Schols, H. A., Kabel, M. A. & Gruppen, H. (2013). Characterisation of cell
643 wall polysaccharides from rapeseed (Brassica napus) meal. *Carbohydrate Polymers, 98(*2),
644 1650–1656.

645 Reinders, G. & Thier, H.-P. (1999). Non-starch polysaccharides of tomatoes I. Characterizing
646 pectin and hemicelluloses. *European Food Research and Technology, 209,* 43–46.

647 Renard, C. M. (2005). Effects of conventional boiling on the polyphenols and cell walls of
648 pears. *Journal of the Science of Food and Agriculture, 85(*2), 310–318.

649 Renard, C. M. & Thibault, J.-F. (1993). Structure and properties of apple and sugar-beet
650 pectins extracted by chelating agents. *Carbohydrate Research, 244(*1), 99–114.

651 Saulnier, L. & Thibault, J.-F. (1987). Extraction and Characterization of Pectic Substances
652 from Pulp of Grape Berries. *Carbohydrate Polymers, 7,* 329–343.

653 Schieber, A., Stintzing, F. & Carle, R. (2001). By-products of plant food processing as a
654 source of functional compounds — recent developments. *Trends in Food Science &*
655 *Technology, 12(*11), 401–413.

656 Seymour, G., Colquhoun, I. J., Dupont, M., Parsley, K. & Selvendran, R. (1990).
657 Composition and structural features of cell wall polysaccharides from tomato fruits.
658 *Phytochemistry, 29,* 725–731.

659 Villanueva-Suárez, M. J., Redondo-Cuenca, A., Rodríguez-Sevilla, M. D. & de las Heras
660 Martínez, M. (2003). Characterization of Nonstarch Polysaccharides Content from Different
661 Edible Organs of Some Vegetables, Determined by GC and HPLC: Comparative Study.
662 *Journal of Agricultural and Food Chemistry, 51(*20), 5950–5955.

663 Wheightman, R., Renard, C., Thibault, J.-F. (1995). Structure and properties of the
664 polysaccharides from pea hulls. Part 1: Chemical extraction and fractionation of the
665 polysaccharides. *Carbohydrate Polymers*, *26*, 121–128.

666 Wennberg, M. S., Engqvist, G. M. & Nyman, E.-L. (2003). Effects of Boiling on Dietary
667 Fiber Components in Fresh and Stored White Cabbage (*Brassica oleracea* var. capitata).
668 *Journal of Food Science, 68(*5), 1615–1621.

669 Westereng, B., Michaelsen, T. E., Samuelsen, A. B. & Knutsen, S. H. (2008). Effects of
670 extraction conditions on the chemical structure and biological activity of white cabbage
671 pectin. *Carbohydrate Polymers, 72(*1), 32–42.

672 Willats, W. G., Knox, J. P. & Mikkelsen, J. D. (2006). Pectin: new insights into an old
673 polymer are starting to gel. *Trends in Food Science & Technology, 17(*3), 97–104.

674 Yapo, B. M., Robert, C., Etienne, I., Wathelet, B. & Paquot, M. (2007). Effect of extraction
675 conditions on the yield, purity and surface properties of sugar beet pulp pectin extracts. *Food*
676 *Chemistry, 100(*4), 1356–1364.

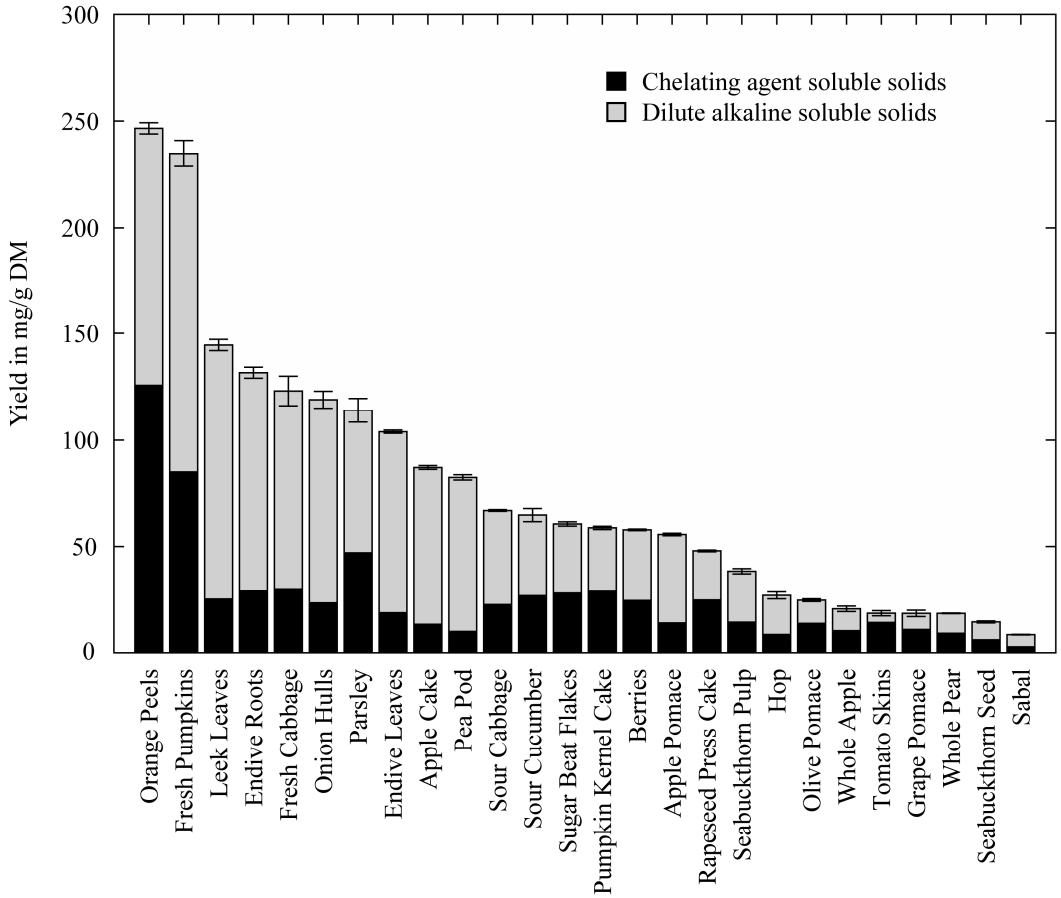
677 Yoo, S.-H., Lee, B.-H., Lee, H., Lee, S., Bae, I. Y., Lee, H. G., et al. (2012). Structural
678 Characteristics of Pumpkin Pectin Extracted by Microwave Heating. *Journal of Food Science,*
679 *77(*11), C1169–C1173.

680 Zykwinska, A., Boiffard, M.-H., Kontkanen, H., Buchert, J., Thibault, J.-F. & Bonnin, E.
681 (2008). Extraction of Green Labeled Pectins and Pectic Oligosaccharides from Plant
682 Byproducts. *Journal of Agricultural and Food Chemistry, 56(*19), 8926–8935.

683

684

685



686

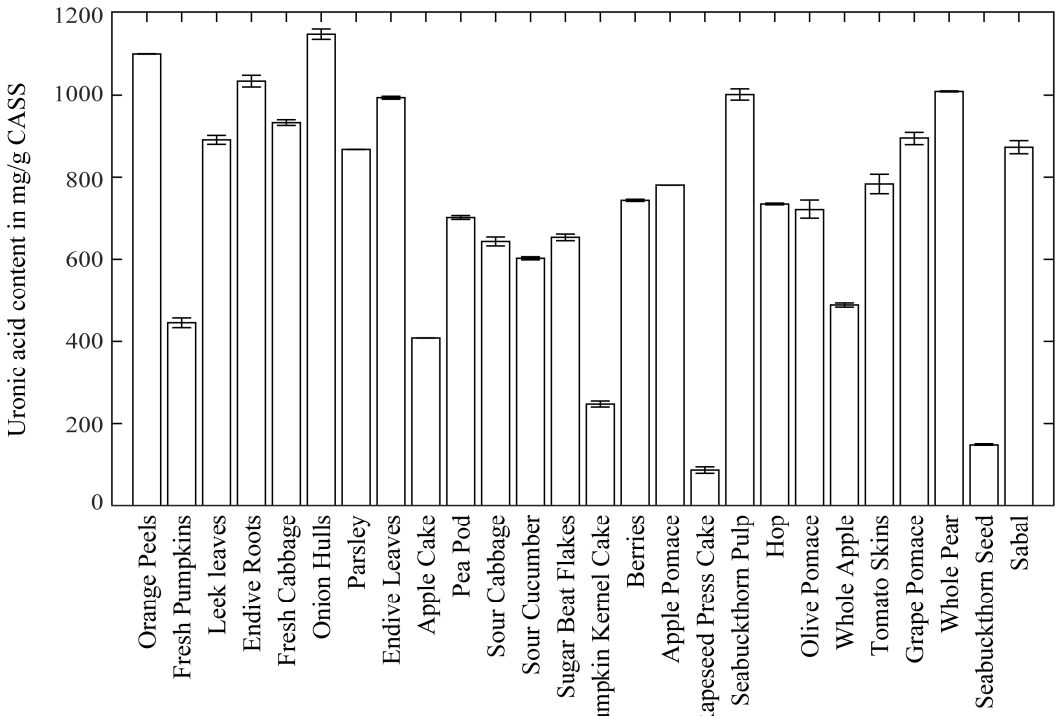
687

688

689 Fig. 1

690

691



692

693

694

695 Fig. 2

696

697

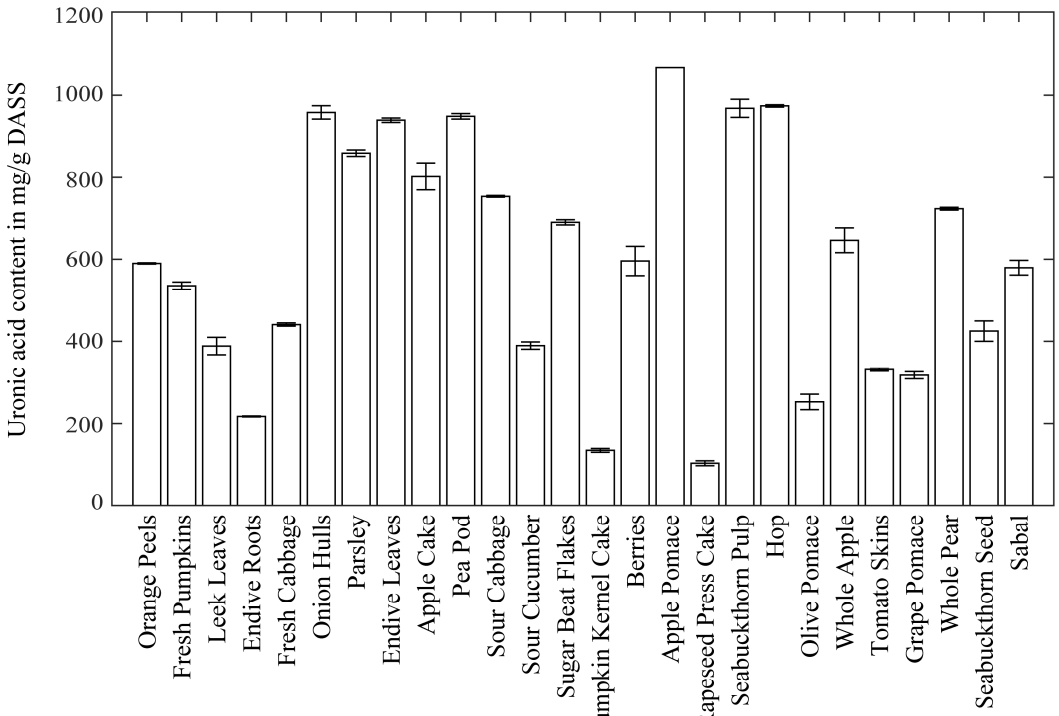
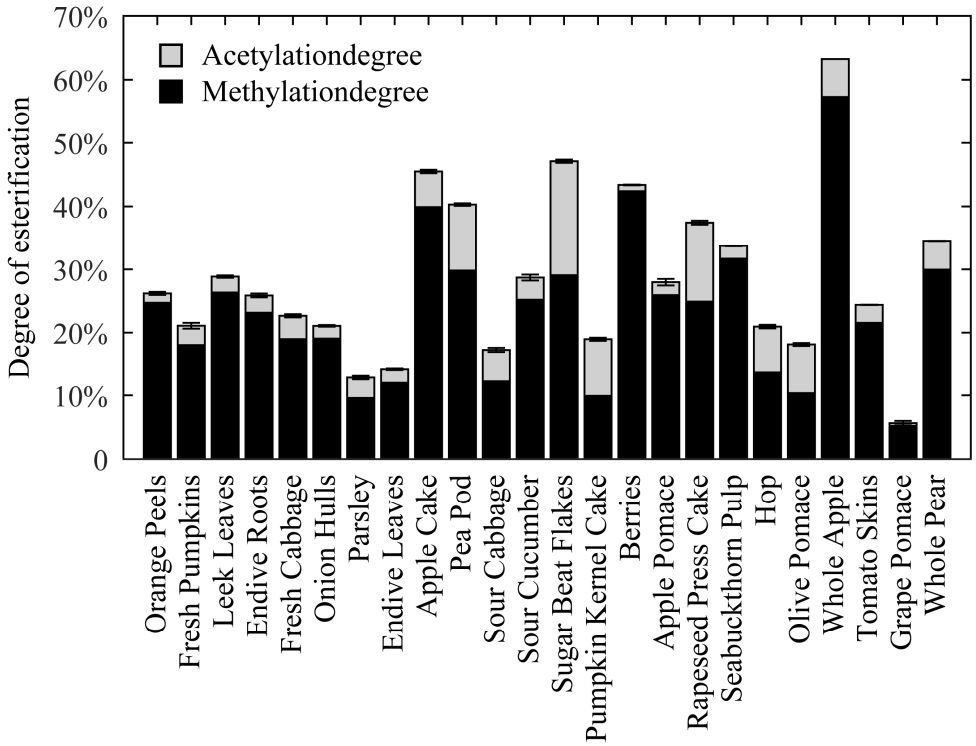


Fig. 3



704

705

706

707 Fig. 4

708

709

710 **Table 1 Profile and content of neutral sugars in CASS (calcium-bound pectin) and DASS (dilute alkaline soluble pectin)**

		Ara (mg/g pectin)		Glc (mg/g pectin)		Rha (mg/g pectin)		Glu (mg/g pectin)		Man (mg/g pectin)		Xyl (mg/g pectin)		Rib (mg/g pectin)	Fuc (mg/g pectin)	
Orange peels	CASS	136	± 10	35	± 6	18	± 4	11	± 4	traces		5	± 1	-	-	
	DASS	266	± 38	105	± 22	37	± 9	10	± 1	1	± 0	5	± 0	-	-	
Fresh pumpkins	CASS	32	± 25	12	± 4	16	± 11	10	± 4	-		26	± 30	-	-	
	DASS	17	± 2	16	± 1	16	± 1	16	± 1	-		13	± 1	-	-	
Leek leaves	CASS	17	± 1	21	± 2	7	± 1	6	± 1	-		3	± 0	-	-	
	DASS	12	± 7	19	± 9	10	± 6	2	± 2	2	± 3	1	± 1	-	-	
Endive roots	CASS	31	± 1	13	± 3	14	± 1	6	± 1	5	± 1	-		-	-	
	DASS	22	± 8	7	± 2	8	± 4	1	± 1	-		1	± 0	-	-	
Fresh cabbage	CASS	54	± 6	64	± 10	23	± 4	20	± 6	-		12	± 1	-	-	
	DASS	195	± 21	158	± 14	39	± 13	21	± 1	4	± 0	26	± 2	-	-	
Onion hulls	CASS	14	± 0	38	± 18	20	± 4	18	± 2	-		-		-	-	
	DASS	13	± 5	107	± 24	21	± 6	13	± 5	-		-	±	-	-	
Parsley	CASS	65	± 3	65	± 1	23	± 1	17	± 0	-		3	± 0	-	2	± 0
	DASS	108	± 10	131	± 8	36	± 4	20	± 1	-		8	± 0	-	5	± 0
Endive leaves	CASS	20	± 1	12	± 1	21	± 0	5	± 1	5	± 0	4	± 1	-	3	± 0
	DASS	36	± 8	20	± 5	33	± 6	5	± 1	7	± 2	6	± 1	-	6	± 1
Apple cake	CASS	58	± 15	27	± 2	11	± 1	27	± 1	-		27	± 5	-	-	
	DASS	85	± 7	26	± 1	22	± 1	16	± 1	-		-		-	-	
Pea pod	CASS	129	± 2	29	± 1	31	± 4	14	± 2	-		107	± 2	-	-	

	DASS	77	± 28	16	± 5	19	± 13	1	± 2	-		36	± 18	-		-	
Sour cabbage	CASS	145	± 1	44	± 5	40	± 1	38	± 0.	-		-		-		-	
	DASS	195	± 45.51	63.47	± 8	41	± 9	22	± 4	-		20	± 2	-		-	
Sour cucumber	CASS	19	± 0.06	39.64	± 1	8	± 2	7	± 1	16	± 2	13	± 0	-		-	
	DASS	35	± 1.74	122.73	± 7	17	± 1	7	± 1	45	± 1	26	± 9	-		-	
Sugar beat flakes	CASS	298	± 24.93	44.04	± 0	36	± 3	7	± 2	-		-		-		-	
	DASS	266	± 74.65	50.16	± 5	25	± 9	5	± 3	-		-		-		-	
Pumpkin kernel cake	CASS	32	± 5.44	17.00	± 4	21	± 1	24	± 2	-		32	± 3	-		-	
	DASS	29	± 2.13	22.68	± 1	22	± 3	33	± 1	-		36	± 1	-		-	
Berries	CASS	40	± 11.39	92.78	± 35	14	± 5	36	± 41	-		-		-		-	
	DASS	26	± 2.44	30.16	± 6	14	± 2	15	± 2	-		-		-		-	
Apple pomace	CASS	73	± 16.07	21.33	± 2	39	± 3	73	± 3	12	± 3	9	± 13	-		-	
	DASS	67	± 2.73	16.91	± 1	35	± 0	55	± 2	-		6	± 5	-		-	
Rapeseed press cake	CASS	76	± 5.43	17.75	± 1	9	± 1	10	± 1	8	± 1	30	± 1	-		9	± 2
	DASS	68	± 18.87	18.09	± 6	8	± 2	9	± 2	9	± 2	21	± 4	5	± 2	11	± 6
Seabuckthorn pulp	CASS	97	± 50.21	9.92	± 4	12	± 6	6	± 3	-		8	± 4	5	± 3	-	
	DASS	75	± 9.05	16.45	± 1	11	± 0	15	± 0	-		9	± 1	7	± 2	-	
Hop	CASS	43	± 9.84	24.47	± 4	16	± 4	8	± 2	10	± 2	27	± 10	-		3	± 1
	DASS	35	± 25.41	19.75	± 14	15	± 13	6	± 6	8	± 6	11	± 7	-		3	± 2
Olive pomace	CASS	159	± 15.84	20.87	± 7	53	± 7	34	± 23	-		18	± 11	-		20	± 17
	DASS	220	± 30.98	27.83	± 3	61	± 11	28	± 4	11	± 2	26	± 18	-		-	
Whole apple	CASS	79	± 14.06	24.39	± 16	15	± 3	16	± 2	9	± 5	47	± 17	-		7	± 0
	DASS	88	± 12.21	38.46	± 8	20	± 3	10	± 2	-		20	± 6	-		3	± 1
Tomato skins	CASS	19	± 2.99	38.85	± 0	8	± 0.4	7	± 1	16	± 0	13	± 2	-		-	

	DASS	29	± 9.15	102.94	± 9	14	± 3	6	± 3	38	± 11	23	± 13	-	-
Grape pomace	CASS	12	± 3.24	8.13	± 2	10	± 2	3	± 1	-		6	± 2	-	-
	DASS	15	± 3.07	9.63	± 3	10	± 2	12	± 1	6	± 1	8.89	± 1	-	-
Whole pear	CASS	64	± 8.92	14.35	± 1	25	± 2	8	± 1	6	± 0	19.81	± 2	-	-
	DASS	99	± 1.19	29.87	± 2	32	± 1	10	± 6	-		37.26	± 15	-	-

711

712

713 **Highlights**

714 - Calcium bound and covalently linked pectin analyzed in 26 food waste streams
715 - Uronic acid content, neutral sugars, acetylation and methylation degree determined
716 - Very wide diversity of pectin structures among vegetal food waste materials
717 - First wide database of pectin content and characterization

718