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Study on dietary fibre by Fourier transform-infrared spectroscopy and chemometric methods

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ABSTRACT

Fresh fruit is an important part of the diet of people all over the world as a significant source of water, vitamins and natural sugars. Nowadays it is also one of the main sources of dietary fibre. In fruit the dietary fibre is simply cell wall consisting essentially of polysaccharides. The aim of present study was to predict the contents of pectins, cellulose and hemicelluloses by partial least squares regression (PLS) analysis on the basis of Fourier transform-infrared (FT-IR) spectra of fruit cell wall residue. The second purpose was to analyse the composition of dietary fibre from fruit based on FT-IR spectral information in combination with chemometric methods (principle components analysis (PCA) and hierarchical cluster analysis (HCA)). Additionally the contents of polysaccharides in studied fruits were determined by analytical methods. It has been shown that the analysis of infrared spectra and the use of multivariate statistical methods can be useful for studying the composition of dietary fibre.

1. Introduction

The plant cell wall is a dynamic structure composed mostly of polysaccharides with high molecular weight. The polysaccharides – cellulose, hemicelluloses and pectins are considered as compartments of dietary fibre originating from the primary cell wall and middle lamella. The dietary fibre may also consist of non-polysaccharide components originating from the secondary cell wall such as lignin, cutin, waxes and suberin (Ha, Jarvis, & Mann, 2000). Dietary fibre is often classified as water soluble and insoluble. Water-soluble fibre includes pectins, some hemicelluloses and gums. Cellulose, lignin and some hemicelluloses are examples of dietary fibre classified as insoluble (Gropper & Smith, 2013, Chapter 4). Fresh fruit is an important part of the human diet all over the world as a significant source of water, vitamins and natural sugars and nowadays it is also the main source of dietary fibre (Li et al., 2013). It is generally accepted that a diet rich in fibre is beneficial to health. Among other things it could protect against constipation, colon diverticulosis, carcinoma of the large bowel and stomach, type 2-diabetes, metabolic syndrome and cardiovascular disease (Anderson et al., 2009; Parkar et al., 2010).

The structure of pectins can be extremely heterogeneous between plants, tissues, and even within a single cell wall. Three major pectic polysaccharides are acknowledged: homogalacturonan (HG), rhamnogalacturonan I (RGI) and rhamnogalacturonan II (RGII). Their backbone contains acidic sugars, mainly galacturonic acid (GalA), to which neutral sugars (ex. rhamnose, galactose, arabinose) could be attached as residues (Taiz & Zeiger, 2003, Chapter 15; Willats, Knox, & Mikkelsen, 2006). Homogalacturonan, also known as polygalacturonic acid or pectic acid, is made up of (1→4)-linked α-D-galacturonic acid (GalA) with occasional rhamnosyl residues that cause a kink in the chain. The carboxyl residues are often methyl esterified. Rhamnogalacturonan I (RG I) is a very large and heterogeneous pectin, with a backbone of alternating (1→4)α-D-galacturonic acid (GalA) and (1→2)α-D-rhamnose (Rha). Side chains are attached to rhamnose and are composed principally of arabinans. Rhamnogalacturonan II is a highly branched pectic polysaccharide, which contains at least ten different sugars in a complicated pattern of linkages (Taiz & Zeiger, 2003, Chapter 15). The characteristic feature of pectic polysaccharides is their ability to form gels due to crosslinking by calcium ions, or by hydrogen bonding between free carboxyl groups on the pectin molecules and also between the hydroxyl groups of neighbouring molecules (Sundar Raj, Rubila, Jayabalan, & Ranganathan, 2012). Therefore, in the food industry pectins are known primarily as a

Abbreviations: CWM, cell wall material; CDTA, trans-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetate; NDF, neutral detergent fibre; ADF, acidic detergent fibre; GalA, galacturonic acid; PLS, partial least square regression; HCA, hierarchical cluster analysis; PCA, principal component analysis.

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gelling agent and are widely used in the production of jams and jellies, fruit juice, confectionary products and bakery fillings (Thakur, Singh, & Handa, 1997). The other major use of pectin is for the stabilization of acidified milk drinks and yogurts (Willats, Knox, & Mikkelsen, 2006).

Cellulose chain is a polymer of β-linked glucose residues arranged in linear chains. The extended glucan chain polymer forms a flat ribbon-like structure that is further stiffened by Van der Waals forces, as well as intra- and intermolecular hydrogen bonds, leading to a regular crystalline arrangement of glucan chains. In nature, cellulose never occurs as a single chain, but exists from the moment of its synthesis as a crystalline array of many parallel, oriented chains – microfibrils – which are its fundamental structural units (Szymańska-Chargot, Cybulska, & Zdunek, 2011). The glucan chain length (degree of polymerisation) varies from about 2000 to more than 25000 glucose residues (Brown, Saxena, & Kudlicka, 1996; Cousins & Brown, 1995). These chains are long enough (about 1 to 5 μm long) to extend through multiple crystalline and amorphous regions within a microfibril. Within the crystalline domains, adjacent glucans are highly ordered and bonded to each other by noncovalent bonding, such as hydrogen bonds and hydrophobic interactions (Taiz & Zeiger, 2003, Chapter 15). Hemicelluloses are a group of polysaccharides with branched chains. The composition of hemicelluloses depends on the source: type of plant and plant tissue. Xyloglucan is the most abundant hemicellulose with the same D-glucose backbone as cellulose (Taiz & Zeiger, 2003, Chapter 15). However, unlike cellulose it has short side chains that consist of monosaccharides. Hemicelluloses seem to form hydrogen bonds with cellulose microfibrils. In this way hemicellulose-cellulose matrix is created. Both hemicellulose and cellulose cannot be digested by humans due to the lack of an enzyme (hydrolase) which destroys the β-glycosidic bonds of cellulose. Despite this, they are found in many applications in industry, for example: cellulose as a dietary fibre-rich food additive in bread or frozen desert or as a tablet filler in medicines; whereas hemicelluloses are used as stabilizers or thickeners.

The characterisation of individual polysaccharides in native plant cell wall is still very complicated due to similarity in the chemical structure of these polymers. To overcome this obstacle a sequential extraction of an individual group of polysaccharides is possible. For this purpose the van Soest method is frequently applied (Chen et al., 2010; Van Soest, 1963). For analysis of extracted fractions FT-IR spectroscopy is widely used, which provides information about the sample components' structure. So far, mainly pectin (Gnanasambandam, 2000; Synytsya, Čopıková, Matějka, & Machovič, 2003), hemicelluloses (Kačuráková, Capek, Sasinková, Wellner, & Ebringerová, 2000), polysaccharide food additives (Černá et al., 2003) or wood cell walls (Chen et al., 2010; Hori & Sugiyama, 2003) have been studied. In our previous work, the FT-IR spectroscopy of the cell wall and chemometric methods were used to examine, quantitatively and qualitatively, the composition of the cell wall material from apples during development. (Szymańska-Chargot, Chylińska, Kruk, & Zdunek, 2015). It was proven that FT-IR spectroscopy combined with chemometric methods as principal component analysis (PCA) or partial least square regression (PLS) is a simple and fast method of determining cell wall material composition (Szymańska-Chargot & Zdunek 2013; Szymańska-Chargot et al., 2015). However, to the best of our knowledge, this approach has never been used to determine the dietary fibre fractions obtained, according to the van Soest method, from fully ripened fruit. So far the only enzymatic-gravimetric methods approved by AACC International were developed for dietary fraction evaluation (McCleary et al., 2011). However, these methods demand long extraction times and are relatively expensive. Here, we propose a method based on FT-IR spectra supported by chemometric analysis and validated by the van Soest method of dietary fibre determination.

Hence, the aim of this study was to predict the contents of pectins (GalA), cellulose and hemicelluloses by partial least squares regression (PLS) analysis of FT-IR spectra of fruit cell wall material.

The second purpose of the present study was to identify chemical and spectral differences in cell wall composition among various fruits using composition analysis of the samples and FT-IR spectral information in combination with chemometric tools, namely principal component analysis and hierarchical clusters analysis.

2. Materials and methods

In the experiment batches of 16 different fruit were investigated. The material, purchased at a local supermarket, was as follows: apple (*Malus domestica*, cv. Szampion), apricot (*Armeniaca Scop*, cv. Bulida), avocado (*Persea*, cv. Fuerte), cherry (*Cerasus*, cv. Łutówka), cucumber (*Cucumis*, cv. Atos), currant (*Ribes rubrum*, cv. Ribesrubrum), grapefruit (*Citrus paradisi Macfad.*, cv. Rio – Red), kiwi (*Actinidia*, cv. Erika), lemon (*Citrus limon*, cv. Verna), melon (*Cucumis melo*, cv. Galia), nectarine (*Prunus persica var. nectarina*, cv. Redgold), orange (*Citrus*, cv. Navelina), peach (*Persica*, cv. Redhaven), strawberry (*Fragaria ananassa*, cv. Clery), sweetcherry (*Prunus avium*, cv. Regina), watermelon (*Citrullus*, cv. Bingo).

2.1. Cell wall material extraction

Cell wall material (CWM) for study was obtained using the hot alcohol insoluble solids method with a few modifications as described previously (Cybulska, Zdunek, Psonka-Antonczyk, & Stokke, 2013; Renard, 2005; Szymańska-Chargot & Zdunek 2013).

2.2. Extraction of dietary fibre fractions from CWM

2.2.1. Hemicellulose and cellulose

Van Soest (Van Soest, 1963) analysis with some modifications was used for cellulose and hemicelluloses determination (Scheme is attached as Supplementary material 1). The Van Soest method enables separation of plant cell wall fractions and thus dietary fibre fractions, by usage of two detergents: a neutral detergent (ND) solution (sodium dodecyl sulphate, EDTA, pH 7.0) removes pectic polysaccharides and in the second step of extraction an acidic detergent (AD) solution (cetyltrimethyl ammonium bromide in 1 N H_2SO_4) removes hemicelluloses. In the primary cell walls (containing no lignin) the NDF (neutral detergent fibre) fraction/residue consists of hemicellulose and cellulose, whereas the ADF (acidic detergent fibre) fraction/residue contains only cellulose.

Three replicates (each approximately 0.1 g) from every CWM sample were taken and placed into a glass crucible for van Soest analysis. Thermogravimetric analysis was performed with a crude fibre extractor FIWE 3 (Velp Scientifica, Italy). Samples were boiled in ND solution (100 mL) for 1 h, then washed by hot water and acetone and finally dried at 105 °C overnight to obtain the NDF fraction.

To extract pure cellulose the procedure was the same except that samples were boiled in AD solution to obtain the ADF fraction.

The hemicellulose yield was estimated according to the following equation:

$$\text{Hemicelluloses } [\text{g}/100\ \text{g}] = \frac{m_{NDF} - m_{ADF}}{m_{CWM}} \cdot 100, \quad (1)$$

and similarly cellulose:

$$\text{Cellulose } [\text{g}/100\ \text{g}] = \frac{m_{ADF}}{m_{CWM}} \cdot 100. \quad (2)$$