DETERMINATION OF MAJOR SUGARS IN FRESH AND DRIED SPICES AND VEGETABLES USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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Abstract

Carbohydrates are one of the most important energy sources in plants synthesized during photosynthesis. They are important for plants to grown and produce. Polysaccharide content changes depending on plant type, growing location and weather conditions. The highest content differs in roots and leaves- photosynthesis starts in leaves, but to grow and produce mostly carbohydrates are localized in roots. It is important to follow up in differences between sugars changes in vegetable and spices. There are many researches focusing on sugar changes mostly in fruits and cereals, less in vegetables, herbs, and spices. The aim of this research was to determine major sugars in nine spices and vegetables- celery (*Apium graveolens var dulce*), parsley (*Petroselinum crispum*), dill (*Anethum graveolens*), leek (*Allium ampeloprasum* L.), garlic (*Allium sativum* L.), onion (*Allium cepa*), celery root (*Apium graveolens var. rapaceum*), pumpkin (*Curcubica maxima*), carrot (*Daucus carota*) grown in Latvia in 2013. Analyses were made using high performance liquid chromatography (HPLC) in the laboratories of Latvia University of Agriculture, Faculty of Food Technology for fresh samples and samples dried in convective dryer at 45±1 °C temperature. Fructose, glucose, sucrose and maltose content was determined using HPLC method, and moisture content in each sample was established by drying samples till constant weight. Results were expressed as grams per 100 grams of dry weight (DW). Analysing obtained results the highest total sugar content was found in vegetable roots (carrot), lowest- in spices' leaves. Convective drying at 45±1 °C process takes from 12 till 48 hours to reduce moisture content. After drying process in most cases individual sugar content increased significantly. During drying process water is removed from samples, sugars are changing, which may indicate possible Maillard reaction.

Keywords: spices, vegetables, drying, sugars, HPLC.

Introduction

By culinary definition vegetables are edible plant parts including stems and stalks, roots, tubers, bulbs, leaves, flowers, some fruits and seeds (Pennington, Fisher, 2009).

Vegetables are an important part of our diet. They provide not only the major dietary fibre component in our food, but also a range of micronutrients, including minerals, vitamins and antioxidant compounds, such as carotenoids and polyphenols (Singh et al., 2012). Most vegetables are commonly cooked before being consumed. Cooking induces significant changes in chemical composition, affecting the bio accessibility and the concentration of nutrients and health-promoting compounds (Mazzeo et al., 2011).

Health beneficial attributes of spices have the potential of a possible therapeutically exploitation in a variety of disease conditions. Spices do not contribute significantly to the nutrient makeup of food, especially because of their small quantities encountered in diet (Srinivasan, 2005). Spices can be added to foods in several forms: as whole spices, as ground spices, or as isolates from their extracts. Spices are aromatic and pungent food ingredients (Suhaj, 2006).

Carbohydrates are divided into following groups- monosaccharides (simple sugars that are the simplest members of carbohydrates, cannot be subjected to hydrolysis); oligosaccharides (consists of small number of monosaccharides, usually two to ten molecules, with disaccharides being the most common in foods; polysaccharides (consists of large amount of monosaccharides). They vary in their physical and chemical properties compared to monosaccharides. Most important polysacharides in food are starch, glycogen and cellulose (Tzia et al., 2012). The final products of carbohydrate digestion in the digestive tract are almost entirely glucose, fructose, and galactose. Because glucose is the only carbohydrate that can be oxidized in muscle, much of the fructose and all of galactose are transported to the liver, after absorption from the intestinal tract, and converted into glucose. The conversion of fructose and galactose occurs in the liver at relatively low rates (Campbell, 2013). Simple monosaccharides such as glucose can be directly absorbed by the host. Disaccharides such as maltose, lactose and sucrose can be hydrolyzed to their respective monosaccharides, but the ability to digest complex plant polysaccharides such as inulin, pectin and xylan is very limited (Ibrahim, Anishetty, 2012).

One of the oldest methods for food preservation is drying, which consists of removing water from the product in order to provide microbiological safety and the most popular drying method is air-drying in convective drier. In this method the drying agent supplies heat to the material and removes moisture from material at the same time (Nawirska et al., 2009). Major disadvantages of hot air drying of foods are low energy efficiency and long drying time during the falling rate period. Because of the low thermal conductivity of food materials in this period, heat transfers to the inner sections of foods during conventional heating is limited (Wang, Xi, 2005). The drying time of the convective technique can be shortened using higher temperatures which increase moisture diffusivity and by cutting the material into smaller pieces. Increased drying temperature entails higher costs and may cause biochemical changes that degrade the dried product quality (Figiel, 2009)

High temperatures can destroy enzymes, vitamins and determine the rancidity of fat-containing foods, but also can lead to the production of free radical scavenging substances, such as Maillard reaction products (Melanoidins and Amadori rearrangement products). Both reactions induced by the transformation can take place simultaneously and can influence each other (Dini et al., 2013). The Maillard reaction is a complex series of reactions that involve reducing sugars and proteins, giving multitude of end products that are known as Advanced Glycation End products. They can contribute to the pathogenesis of diabetes and neurological diseases such as Alzheimer's disease. And also play a major role in vascular stiffening, atherosclerosis, osteoarthritis, inflammatory arthritis and cataracts (Edeas et al, 2010)

The aim of this research was to determine major sugars (fructose, glucose, sucrose and maltose) in nine spices and vegetables – celery, parsley, dill, leek, garlic, onion, celery root, pumpkin, carrot grown in Latvia in 2013. From obtained results was determined drying impact on sugars content.

Materials and Methods

All samples were grown and harvested reaching full maturity in Latvia in 2013. Analyses were made in the laboratories of Latvia University of Agriculture, Faculty of Food Technology.

Fresh samples were washed and cut in equal small pieces. For drying samples were washed, cut in small pieces and dried in a convective dryer with fan (Memmert, Model 100-800) at 45±1 °C temperature till constant (not changing) mass.

For samples moisture content was determined according to AOAC (1995). Samples were dried at 105±1 °C: fresh samples for 2 hours and dried samples for 30 minutes. Analysis were triplicated. Moisture content was expressed as percentes. From moisture was calculated dry matter.

Sugars content (fructose, glucose, sucrose and maltose) was determined using high performance liquid chromatography (HPLC) method (Shimadzu LC 20 Prominence) (Rybak-Chmielewska, 2007; Dimins et al., 2008; Beitane et al., 2013). Method is based on chromatographic separation of sugars and their retention time. Sample extracts were made to extract sugars according to following procedure- samples were blended in small particles (using commercial blender for fresh samples – Bosch MSM 6700 or coffee mill for dried samples – Scarlett SL-1545 Silver Line), soaked in water and extracted in ultrasound bath (SELECTA P ULTRASONS) at 35±1 °C for 45 minutes. Solution was filtrated twice using filter paper and 0.45 μm Millipore membrane.

The analysis by HPLC were performed at 25±1 °C under isocratic conditions. The mobile phase consisted from A – acetonitrile; B – water (70:30). Flow rate was 1.00 mL min^{-1} and injection volume was 10 μL. The analytic column Alltech-NH_2 (4.6 mm×250 mm×5 μm) was used and refractive index detector (RID-10A) was used. Total time of analysis was up to 30 min. The identification of sugars in vegetables and spices was done by comparing retention times of individual sugars in the reference vs. tested solution (qualitative analysis). The quantitative assays were made by the following carbohydrates: fructose, glucose, sucrose and maltose. The content of those compounds were assessed based on the comparing peak areas obtained from the reference analysis. Analysis was done duplicate. Results were expressed as grams per 100 g of dry weight (g 100 g^{-1} DW).

Results and Discussion

The highest dry matter content among fresh samples was established in garlic, lowest – in onion. In dried samples dry matter content was higher than in fresh samples (Table 1).

Table 1

Dry mater content in fresh and dried vegetables and spices

Samples	Dry matter in fresh samples,%	Dry matter in dried samples,%
Celery	17.57±0.18	90.66±0.91
Parsley	25.30±0.25	91.22±0.91
Dill	18.40±0.18	93.04±0.93
Leek	11.07±0.11	87.33±0.87
Onion	6.20±0.06	78.92±0.79
Garlic	45.59±0.46	87.44±0.87
Celery root	12.96±0.13	90.46±0.90
Carrot	11.60±0.12	84.87±0.85
Pumpkin	8.21±0.08	89.14±0.89

Dried onion, leek, garlic, carrot and pumpkin are samples which can absorb water from air in short time during grinding process.

Fructose and glucose content increased after drying in all samples (Table 2). All results are expressed as grams per 100 g dried weight (g 100 g^{-1} DW).

Increasing can be explained with polysaccharide reducing in smaller monomers. Vegetables and spices contain a large amount of poly carbohydrates.

The highest fructose content was determined in dried onions, lowest in fresh garlics. After drying process in most cases fructose content increases significantly ($p<0.05$). Only pumpkins fructose content decreases. The highest glucose content was reached in dried celery roots, lowest was in fresh garlics. Glucose content in most cases increases significant ($p<0.05$). Glucose content in pumpkins decreases significant ($p<0.05$).

Comparing reached data to USDA Nutrient database, glucose content in carrots are 0.28 g 100 g^{-1} fresh weight (FW), in onions – 1.97 g 100 g^{-1} FW, in celery 0.55 g 100 g^{-1} FW, in dried parsley 2.76 g 100 g^{-1} DW, in dried onion 0.73 g 100 g^{-1} DW, in dried garlic 0.07 g 100 g^{-1} DW. Fructose content in carrots are 0.26 g 100 g^{-1} FW, in onions 1.26 g 100 g^{-1} FW, in celery 0.51 g 100 g^{-1} FW, in dried parsley 0.42 g 100 g^{-1} DW, in dried onion 1.67 g 100 g^{-1} DW, in dried garlic 0.31 g 100 g^{-1} DW. According to Shanmugavelan et al. (2013), fructose content in onions are 27.74 g 100 g^{-1} DW, in carrots 11.24 g 100 g^{-1} DW. Glucose in onions 31.80 g 100 g^{-1} DW, in carrots 10.37 g 100 g^{-1} DW. According to Caruso et al. (2014) reached data glucose content in onions are 27.8 g 100 g^{-1} DW and fructose are 21.5 g 100 g^{-1} DW. Obtained results can be compared with literature data.

Table 2

Fructose and glucose content in fresh and dried vegetables and spices

Samples		Fructose, g 100 g^{-1} DW	Glucose, g 100 g^{-1} DW
Celery	A	1.035±0.104	4.619±0.462
	B	1.806±0.181	12.407±1.241
Parsley	A	3.527±0.353	9.219±0.922
	B	5.437±0.544	11.729±1.173
Dill	A	1.089±0.109	2.282±0.228
	B	3.245±0.325	4.411±0.441
Leek	A	12.647±1.265	10.838±1.084
	B	12.232±1.223	13.322±1.332
Onion	A	18.442±1.844	18.094±1.809
	B	26.891±2.689	23.209±2.321
Garlic	A	0.273±0.027	0.097±0.001
	B	1.143±0.011	0.317±0.032
Celery root	A	0.815±0.082	20.586±2.059
	B	1.200±0.120	25.059±2.506
Carrot	A	10.345±1.035	13.161±1.316
	B	14.135±0.141	24.559±1.456
Pumpkin	A	18.867±1.887	17.771±1.777
	B	13.492±1.349	12.837±0.128

A–fresh samples; B–dried samples

The highest sucrose content was determined in dried celery roots, the lowest in fresh dill. The highest maltose content was in dried pumpkins, but not detected in fresh carrots (Table 3).

The highest sucrose content was determined in vegetable roots, less in leaves. Maltose content has no differences between vegetable roots and vegetable leaves in most cases. Content of sucrose and maltose increases significantly ($p<0.05$) after drying.

Comparing reached data to USDA Nutrition database, sucrose content in carrots are 1.92 g 100 g^{-1} FW, in onions 0.99 g 100 g^{-1} FW, in celery 0.11 g 100 g^{-1} FW, in dried parsley 4.09 g 100 g^{-1} DW, in dried onion 3.87 g 100 g^{-1} DW, in dried garlic 2.05 g 100 g^{-1} DW. Maltose content in all previously described has not been detected. According to Shanmugavelan et. al. (2013), sucrose content in onions is 8.32 g 100 g^{-1} DW, in carrots 20.09 g 100 g^{-1} DW. According to Caruso et al. (2014), sucrose content in onions are 11.3 g 100 g^{-1} DW. Maltose content was not analysed in both researches. Obtained results can be compared with literature data.

Table 3

Sucrose and maltose content in fresh and dried vegetables and spices

Samples		Sucrose, g 100 g^{-1} DW	Maltose, g 100 g^{-1} DW
Celery	A	0.707±0.071	0.205±0.021
	B	0.746±0.075	0.712±0.071
Parsley	A	0.353±0.035	0.692±0.069
	B	1.040±0.104	1.275±0.128
Dill	A	0.011±0.001	0.812 ±0.081
	B	0.405±0.041	1.626±0.163
Leek	A	2.152±0.215	0.405±0.041
	B	9.411±0.941	0.888±0.089
Onion	A	1.123±0.112	0.429±0.043
	B	5.274±0.527	0.826±0.083
Garlic	A	2.255±0.226	0.254±0.025
	B	2.709±0.271	0.509±0.051
Celery root	A	11.247±1.125	0.664±0.066
	B	10.260±1.026	0.742±0.074
Carrot	A	23.911±2.391	n.d.
	B	18.019±1.802	1.556±0.156
Pumpkin	A	2.050±0.205	1.088±0.109
	B	6.394±0.639	1.915±0.192

A–fresh samples; B–dried samples; n.d.–not detected

Increasing monosaccharide and disaccharides could be explained by samples possible oligosaccharides division in more simple compounds. According to Yang et.al (2014), the pre-treatment and hydrolysis of celluloses and oligosaccharides can be generated from hydrothermal (steaming, blanching, sterilization, drying etc.) pre-treatment of the cellulose. Using hydrolysis of oligosaccharides fermentable sugars can be recovered. Hydrolysis can be done using acid, alkaline, enzymes and oxidative degradation.

In future research will be analysed polysaccharide changes in fresh and dried vegetables and spices and how they are associated with antioxidant enlargement or reducing.

Conclusions

During drying process fructose, glucose, sucrose and maltose content significantly increased. Increasing may be explained with oligosaccharide dividing in monomers and dimers or during possible Maillard reaction. Catalyst for the decomposition reaction is heat. Spices and vegetables contain lower sucrose and maltose content, but higher fructose and glucose content. Vegetables and spices can be used in diets with low calorie amount than fruits.

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