SIMILARITY OF OIL COMPONENTS IN WASTE BUCKWHEAT FLOUR DETERMINED USING GC-MS

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Abstract: Gas chromatography with mass spectrometry (GC-MS) was used for performing a qualitative analysis of the liposoluble flour extracts of 9 buckwheat samples, taken as leftovers from restaurants. All 9 samples were defatted with hexane, and then those hexane extracts were used for the analysis of the fatty acids of lipid components. Transesterification reagent was TMSH (trimethylsulfonium-hydroxide, 0.2 M in methanol). With this transesterification reaction fatty acids esterified from acilglycerol to methyl-esters. The results show that the dominant methyl-esters of fatty acids are actually very similar in all buckwheat samples. The following cluster analysis was used for the comparison of the liposoluble flour extracts of 9 buckwheat waste flour samples.

Key words: waste buckwheat flour, gas chromatography-mass spectrometry, correlations of liposoluble composition

Introduction

Common buckwheat (*Fagopyrum esculentum* Moench) is an alternative pseudocereal belonging to the *Polygonaceae* family. Buckwheat hulled achenes have received renewed interest due to their high nutritive value, flavonoid content, and suitability for a gluten-free diet. The use of the herb as a medicinal plant is less well-known. An infusion made of *Fagopyri herba* has been administered against high-blood pressure. Herb extracts have been efficiently used against leg edema, and they can protect against diabetic retinopathy, as well. The leaves and delicate buckwheat shoots are consumed as a salad, vegetable or as a heat-processed food, prepared similarly to spinach. In China, India, and Nepal, the leaves are also used as a dried or pickled vegetable. In Japan, buckwheat inflorescences are utilized as a functional food, due to their high rutin content. The green flour obtained by milling the dried flowering buckwheat plants is added as a natural food colorant to pasta, ice cream, and other products in Japan and South Korea. Recently, a new vegetable -buckwheat sprouts- was introduced. It is known that the achenes of buckwheat can be stored for a long time without any symptoms of chemical change. This is due to the content of several natural antioxidants stabilizing the grain during storage. Antioxidants play an important role in preventing undesirable changes in the nutritional quality of foods, and they have an important role in the prevention of human diseases, as well.[1]

The purpose of this study is to quickly and relatively easy determine similarity between 9 types of waste buckwheat flour, taken from different restaurants, by creating the dendrograms of liposoluble extracts.

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Material and methods

About 10 g of each of the following samples were grinded: Godijeva (H1), Bambi (H2), Darja (H3), Francuska (H4), Prekumurska (H5), Češka (H6), Čebelica (H7), Novosadska (H8), and Spacinska (H9). Each sample was homogenized and then treated in the following manner: 0.5 g of flour was poured in 12 mL cuvette for centrifugation with the precision of 0.01 g. The cuvette was additionally filled with 5 mL of n-hexane and stirred on vortex for 2 min, after which the mixture was centrifuged at 2000 rotations/min for 5 min. After this, 3 mL of clear supernatant were poured into a 10 mL glass and left to steam up on the room temperature. The amount of 10 μL was taken from the oily residue, reconstituted to 400 μL of methanol, and additionally 100 μL of the transesterification reagent – TMSH (trimethylsulfonium-hydroxide, 0.2 M in methanol, Marchery-Nagel) were added. With a transesterification reaction, the fatty acids esterified from acilglycerol to methyl-esters.

All the tests were performed on a gas chromatography system. The GC-MS analyses were performed on Agilent Technologies 7890 instrument paired with MSD 5979 equipment (Agilent Technologies, Palo Alto, CA, USA) operating at EI mode at 70 eV. The DP-5 MS column (30 m, 0.25 mm, 25 μm) was used. The temperature program was: 50-130˚C at 30˚C/min and 130-300˚C at 10˚C/min. The injector temperature was 250˚C. The flow rate of the carrier gas (helium) was 0.8 mL/min. The split ratio of 1:50 was used for the injection of 1 μL of the solutions. WILEY 275 library was used for the mass spectrum analysis. PAST program was used for the statistical data processing.[2]

Results and discussion

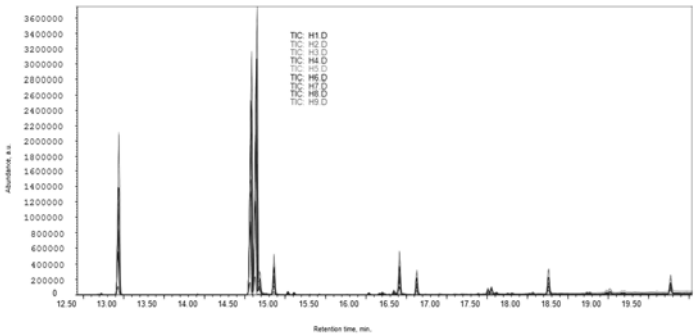
The lipid content of buckwheat seeds varies, depending on the veriety of buckwheat, region in which it is grown, but differences can occur also due to the different time of harvest.[3]

The dominant fatty acids of buckwheat seeds are unsaturated fatty acids (18:1 and 18:2). Linoleic (18:2), oleic (18:1), and palmitic acid (16:0) constitute 88% of the total fatty acids in buckwheat seeds.[4,5]

By comparing the fatty acid composition of common and tartary buckwheat, it can be concluded that the content of saturated acids (16:0 and 18:0) in tartary buckwheat is higher than in common buckwheat, which can be seen in the ratio of unsaturated and saturated fatty acids.[6]

With typically 80% unsaturated fatty acids and more than 40% of fatty acids, such as the polyunsaturated essential fatty acid-linoleic acid[4], buckwheat is nutritionally superior to cereal grains in the fatty acid composition.[7]

Figure 1 presents the chromatogram of the hexane extracts of waste buckwheat samples from 13 to 21.60 min. Chromatograms of all nine samples are very similar. The peak integration shows the ratio of components areas 1:150.



Slika 1. Hromatogrami liposolubilnih (heksanskih) ekstrakata svih uzoraka heljde
Figure 1. Chromatograms of all buckwheat sample components in the liposoluble (hexane) extracts

Table 1 shows the retention time of components in the chromatogram presented in Figure 1.

Tabela 1. Retenciona vremena (R_t) komponenata u liposolubilnim (heksanskim) ekstraktima heljde.
Table 1. Retention time (R_t) of buckwheat components in the liposoluble (hexane) extracts.

Rt/min	Jedinjenje *Compound*
12.940	Hexadecanoic acid, methyl-ester
14.581	9,12-Octadecenoic acid (Z,Z)-, methyl-ester
14.647	9-Octadecenoic acid, methyl-ester
14.864	Octadecanoic acid, methyl-ester
16.419	Eicosenoic acid, methyl-ester
16.632	Eicosanoic acid, methyl-ester
17.51	Unknown
17.56	Unknown
18.264	Docosanoic acid, methyl-ester
19.776	Tetracosanoic acid, methyl-ester

The fatty acids profile of analysed buckwheat species was the same in all nine samples. The following fatty acids have been identified as dominant in the form of methyl-esters: palmitic acid, linoleic acid and oleic acid. The retention time of the three methyl-esters is in the range from 12 to 15 min, Figure 1. These fatty acids and their methyl-esters comprise about 90% of the integrated area of the chromatogram.

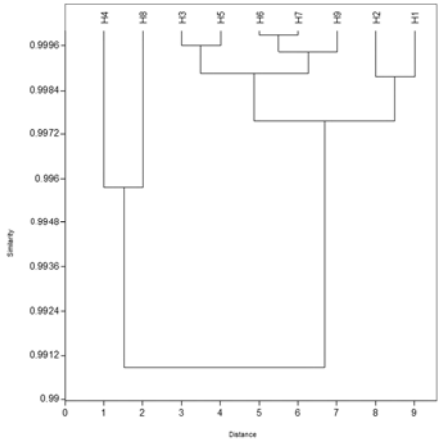
They come only from triglycerides, not from phospholipids, glycolipids, mono- and diglycerides.[8]

Generally, similarity in the composition of lipophilic components was detected in all nine species of buckwheat, which is in the line with previous studies.[9]

The purpose of the study was to identify liposoluble components and also to compare the presence of components in the hexane extract samples of waste buckwheat flour. The cluster analysis was used to compare samples. A single linkage algorithm and similarity measure type of correlation were used.[2]

Figure 2 shows Pearson's r correlation coefficient. The ordinate (Y-axis) presents the correlation coefficient. The X-axis is labelled as a distance and refers to a measurement of the distance between clusters.

The Pearson's r correlation dendrograms show that the similarity in the composition of lipophilic substances of buckwheat (components listed in Table1) is significant ($r > 0.990$), Figure 2.



Slika 2. Dendrogram korelacije komponenata 9 uzoraka heljde iz Tabele 1

Figure 2. Dendrogram of component correlations from Table 1 of 9 buckwheat species

Conclusion

This technique was used for showing that the fatty acids composition of different waste buckwheat flour varieties is very similar, regarding nutritional aspect. These results can be considered for further usage of waste buckwheat flour for other purposes.

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SLIČNOST LIPIDNOG SASTAVA OTPADNOG BRAŠNA HELJDE DOKAZANA PRIMENOM GASNE HROMATOGRAFIJE SA MASENOM SPEKTROMETRIJOM

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Izvod

Za kvalitativnu analizu liposolubilnih komponenata 9 uzoraka otpadnog brašna heljde korišćena je gasna hromatografija sa masenom spektrometrijom (GC-MS). Svih 9 uzoraka prethodno je obezmašćeno heksanom, a potom su heksanski ekstrakti korišćeni za analizu sastava masnih kiselina. Reakcijom transesterifikacije masne kiseline prevedene su iz acil-glicerola u odgovarajuće metil-estre, a kao reagens za transesterifikaciju korišćen je TMSH (trimetilsulfonijum-hidroksid, 0,2 M u metanolu). Rezultati pokazuju da je sastav najzastupljenijih masnih kiselina, odnosno njihovih metil-estara, veoma sličan u svih 9 uzoraka otpadnog brašna heljde. U cilju poređenja liposolubilnog sastava heksanskih ekstrakata uzoraka otpadnog brašna heljde primenjena je klaster analiza.

Ključne reči: otpadno brašno heljde, gasna hromatografija sa masenom spektrometrijom, korelacije liposolubilnog sastava

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