COMPREHENSIVE IDENTIFICATION OF POLYPHENOLS IN DIFFERENT HAZELNUT PRODUCTS

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Abstract – The aim of this study was to identify the polyphenolic profiles of hazelnut products (natural hazelnut, roasted hazelnut, hazelnut skin, and cold press hazelnut oil).

Within the scope of the study, polyphenolic profiles of hazelnut products were analysed tentatively. Q-Exactive LC/MS/MS (orbitrap) was used to tentatively identify the new polyphenolic compounds in hazelnut products and 32 compounds were detected, of which 16 were identified for first time in hazelnut products. The majority of polyphenols were detected in hazelnut skin, while epicatechingallate was the only phenolic compound detected in hazelnut oil. As a result, the present study suggests that hazelnut skin is a good source of polyphenols and can be used as source of functional ingredients.

Keywords: hazelnut, phenolics, phenolic acids

1. INTRODUCTION

Daily consumption of nuts, including hazelnut, was recommended by health claims from Food and Drug Administration (FDA) and European Food Safety Authority (EFSA) for coronary heart disease reduction [1, 2].

Although there are several studies published regarding phenolic compounds of hazelnut and its co-products [3, 4, 5, 6, 7] phenolic profiles of natural and roasted hazelnuts, hazelnut oil as well as roasted hazelnut skin were not identified comprehensively. The aim of this study was to identify phenolic profiles in hazelnut samples by Q-Exactive LC/MS/MS (orbitrap) technique.

2. EXPERIMENTAL

2.1. Samples

The premium class natural (raw), roasted Turkish Tombul hazelnut (*Corylus avellana* L.) and roasted skin, by-product of roasting process, were obtained from Giresun Commodity Exchange (Turkey), at the beginning of the harvest season of 2016. The hazelnut samples were kept in a control cabinet (at 5 °C with relative humidity of 65−70%). Cold press hazelnut oil was produced from natural hazelnut by using press machine.

2.2. Preparation of hazelnut crude extract

Phenolic compounds were extracted from defatted meals as described by Robbins, Gong, Wells, Greenspan, & Pegg [8].

2.3. Extraction and hydrolysis of phenolic acids

Phenolic acids were extracted from freeze-dried extract according to the method described by Robbins et al. [8] with slight modifications. Free, ester-linked and glycoside-linked parts, organic phase was removed under vacuum at 40 °C and then redissolved in methanol, filtered before the analysis performed in Q-Exactive LC/MS/MS (orbitrap).

For hazelnut oil, phenolics were extracted according to the method described by Rotondi, Bendini, Cerretani, Mari, Lercker& Taschi [9] with slight modifications The concentrated extract was freeze-dried.

2.4. Identification and quantification of phenolic profile

Free, ester-linked and glycoside-linked phenolic compounds for each sample were analysed in Q-Exactive LC/MS/MS (orbitrap). Analysis was performed according to Del Rio, Calani, Dall'Asta, and Brighenti [10], with slight modifications. Briefly, 10 µL of sample was injected into the ODS, Hypersil column (250 mm x 4.6 mm, 5 µm, Thermo Scientific, Thermo Scientific, Waltham, MA, USA) with a 0.8 mL/min gradient flow (mobile phase A: 0.1% formic acid-water; mobile phase B: methanol; 0-5 min, mobile phase B concentration changed as 0-9% B; 5-16 min, 9-2% B; 16-35 min, 2-18% B; 35-50 min, 18-20% B; 50-65 min, 20-30% B; 65-80 min, 30% B.

3. RESULTS AND DISCUSSION

The phenolic profiles were screened with a strategy of both target screening (phenolic compounds which were previously reported in hazelnut and its co-products) and suspect screening (phenolic compounds which were previously reported in other tree nuts and their co-products). Among 155 compounds listed in the establish library of Q-Exactive LC/MS/MS (orbitrap), 32 compounds were tentatively identified, 16 of which were identified for the first time in hazelnut samples (Table 1).

In detailed identification of phenolics present in hazelnut samples 32 compounds were tentatively identified, including flavonoids, phenolic acids and related compounds, hydrolysable tannins and related compounds, and others. Roasted hazelnut skin contained the highest content of phenolic acids.

4. CONCLUSIONS

These results indicated that roasted hazelnut skin, which is an excellent source of phenolics, can therefore have potential for use in development of functional food and nutraceutical ingredients.

Table 1. Tentative identification of phenolic compounds in natural, roasted, and roasted hazelnut skin hazelnut by orbitrap.

Peak no	Tentatively identification	Newly identified compound	Sample detected and presence of forms
Flavonoids			
1	(-)-Epicatechin-3-*O*-gallate	Yes	N-E, N-F, O-F, R-F, S-E, S-F, S-G
2	Eriodictyol	Yes	N-E, R-E, S-F
3	Isorhamnetin-3-*O*-rutinoside	Yes	S-F
4	Kaempferol-3-*O*-glucoside	Yes	N-F, R-F, S-E
5	Quercetin	No	R-F
6	Quercetin glucuronide	No	N-F, S-F
7	Quercetin hexoside isomer	No	S-E, S-F, S-G
8	Quercetin-3-*O*-glucoside	No	S-E, S-F, S-G
Phenolic acids and related compounds			
9	3-p-coumaroylquinic acid	Yes	N-G
10	Coutaric acid	Yes	R-E
11	Fertaric acid	Yes	R-E, S-F
12	Neochlorogenic acid	Yes	N-F, R-E
13	Ellagic acid	Yes	N-E, R-E, R-F, S-E
14	Digalloyl-glucose isomer	Yes	N-E, N-F, R-E, R-F, S-F
15	Chlorogenic acid	No	N-F, R-E
16	Gallic acid	No	N-F, N-E, N-G, R-F, R-E, R-G, S-F, S-E, S-G
17	Protocatechuic acid	No	N-F, N-E, N-G, R-F, R-G, S-F, S-E, S-G
18	Salicylic acid	No	N-F, N-G, R-F, R-G, S-F, S-E
19	Syringic acid	No	N-F, N-E, N-G, R-F, R-E, R-G, S-F, S-E, S-G
20	Vanillic acid	No	N-F, N-E, N-G, R-F, R-E, R-G, S-F, S-E, S-G
21	4-Hydroxybenzoic acid	No	N-F, N-G, R-F, R-G, S-F, S-G
22	Caffeic acid	No	N-E, N-G, R-E, S-E
23	Ferulic acid	No	N-F, N-E, N-G,

			R-F, R-E, R-G, S-F, S-E,
24	*o*-Coumaric acid	No	N-F, N-E, N-G, R-F, R-E, R-G, S-F, S-E,
25	Sinapic acid	No	N-F, N-E, N-G, R-F, R-E, R-G, S-F, S-E, S-G
Hydrolysable tannins and related			
26	Ellagic acid hexoside isomer	Yes	N-F, R-E, S-F, S-G
27	Ellagic acid pentoside isomer	Yes	N-F, R-F, S-E, S-G
28	Flavogallonic acid dilactone isomer	Yes	S-E, S-F, S-G
29	HHDP-glucose isomer	Yes	N-F, S-G
30	Valoneic acid dilactone	Yes	S-E, S-F, S-G
Others			
31	Dihydroxycoumarin	Yes	R-E
32	Procyanidin dimer	No	S-F, S-G

Abbreviations: N: natural, R: roasted, and S: skin, O: oil; E: ester-linked, F: free, G: glycoside-linked, HHDP-glucose: bis(hexahydroxydiphenoyl)glucose].

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