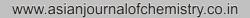
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Mineral Compositions of Herbal Coffees Consumed in Turkey†

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Interest in herbal natural products such as wild vegetables, herbal teas, herbs, spices and herbal mixtures for healthy life has been gradually rising in recent times. Because of their probable side effects on human health, some ordinary foods and drinks are also substituted by healthier or less harmful ones. Because of the distinguished aroma and stimulant effects, different coffee products are of the most used drinks all over the world. Because of its secondary metabolites, mainly caffeine, coffee products have recently been restricted for some people suffering some ailments like cardiovascular diseases. These are also addictive drinks and desired by some people regularly. All the coffee species, coffee arabica, coffee robusta *etc.*, are grown in warm climates. In some years, unexpected climatic factors or political problems in coffee producing countries cause fluctuations in market prices and crop supply. For this reason, because of the fact that people could not find coffee kernels, they use some plants similar to coffee naturally grown in surrounding area. Having rich biodiversity in flora and cultural profundity in various regions, Turkey has a great number of traditional food and drink. Terebinth coffee (*Pistachia terebinthus* L.), black cumin coffee (*Nigella sativa* L.), carob coffee (*Ceratonia siliqua* L.), date coffee (*Phoenix dactylifera*) and gundelia coffee (*Gundelia tournefortii*) are widely consumed herbal coffees in Turkey. Besides their taste and benefit for health, mineral compositions of them are important for food safety. In the present study, some traditional herbal coffees were evaluated for their mineral compositions. Sixteen different minerals (B, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb and S) were detected in the coffee samples. Processed herbal coffees were also compared to their raw materials in terms of mineral compositions.

Key Words: Herbal coffee, Medicinal plants, Minerals, Natural drinks.

INTRODUCTION

Because of adverse side effects of chemicals used in agriculture and food industries, interest in wild edible plants, natural and ecological products used in diets have started to increase in the last decades. This tendency has risen especially in developed countries earlier than the undeveloped ones. Besides huge demand for healthy foods, humans are looking for distinctive taste and aroma in their food and drink customs. Thus, food and drink industries started to diversify their products and enrich their tastes with unique aroma. Nowadays, the most consumed foods and drinks that chemically produced and contain some addictive compounds like caffeine, tein etc. have addictive effects on humans. Their adverse effects for humans' health were also proven and consumers have been trying to give up for them. In this regard, drink industry started to look for novel products in order to maintain their market shares. A number of traditional drinks obtained from natural resources have been consumed all over the world for centuries. Some of them have been produced mainly plant materials such as herb,

leaf, flower, root *etc*. Traditional herbal coffees locally produced and consumed in Turkey are good samples such as natural drinks. The term of herbal coffee can easily defined as hot drinks, which are prepared by frying different parts of various plant parts, other than coffee beans, till brown colour, grinding and cooking like Turkish coffee¹.

Related to interest in traditional organic products and herbal coffees, their industrial production and marketing have started recently. Thus, determining of their chemical properties and effects on human health for food safety and quality aspects has been needed. We could also not find any scientific data about herbal coffees up to now. Our research team started to investigate their chemical and pharmaceutical properties of them. We also published some scientific article recently^{2,3}.

Mineral compositions of foods and drinks used in main diets are important for human health. Determination of mineral compositions both useful and harmful ones in food materials and their raw materials is very important in respect to food safety and human health. Thus, a number of scientific studies for determining mineral compositions of plant materials and 5830 Sekeroglu Asian J. Chem.

| | TABLE-1 SOME CHARACTERISTICS OF PLANT MATERIALS USED FOR HERBAL COFFEES' PRODUCTION | | | | | | | | | | | | | |
|----------------|--|---------------|---------------|------------------------------------|---|------------------------------|--|--|--|--|--|--|--|--|
| Common name | Scientific Name | Local name | Origin | Parts used | Ethnobotanic uses | Pharmaceutical Properties | | | | | | | | |
| Terebinth | Pistachia terebinthus L. | Meneniç | Mediterranean | Fruit, resin | Herbal coffee, snack | Cough, asthma | | | | | | | | |
| Black cumin | Nigella sativa L. | Çörekotu | Mediterranean | Seed | Herbal coffee, bakeries, traditional medicine | All the diseases | | | | | | | | |
| Carob | Ceratonia siliqua L. | Harnup | Mediterranean | Fruit, molasses | Fruit | Good power, aphrodisiac | | | | | | | | |
| Date | Phoenix dactylifera | Hurma | Africa | Fruit, kernel | Fruit, traditional medicine | Good power, aphrodisiac | | | | | | | | |
| Gundelia | Gundelia tournefortii | Kenger | Mediterranean | Fresh plant parts, latex, fruit | Vegetable, gum, herbal coffee | - | | | | | | | | |

| TABLE -2 MINERAL COMPOSITIONS OF HERBAL COFFEES AND THEIR RAW MATERIALS | | | | | | | | | | | | | | |
|--|-------------------|-----------------|-----------------|-----------------|------------------|--|--|--|--|--|--|--|--|--|
| Materials | Cd | Cr | Cu | Ni | Pb | | | | | | | | | |
| HRK | 0.018 ± 0.002 | 5.70 ± 0.31 | 7.53 ± 0.52 | 0.67 ± 0.04 | 0.02 ± 0.01 | | | | | | | | | |
| HRM | 0.019 ± 0.001 | 0.12 ± 0.01 | 7.18 ± 0.19 | 0.68 ± 0.03 | 3.63 ± 0.15 | | | | | | | | | |
| KNK | 0.018 ± 0.001 | 0.16 ± 0.01 | 6.99 ± 0.36 | 0.99 ± 0.03 | 0.09 ± 0.01 | | | | | | | | | |
| KNM | 0.019 ± 0.052 | 22.11 ± 0.26 | 9.79 ± 0.15 | 2.71 ± 0.05 | 13.74 ± 0.25 | | | | | | | | | |
| HMK | 0.007 ± 0.001 | 0.14 ± 0.01 | 7.39 ± 0.28 | 0.26 ± 0.02 | 0.09 ± 0.01 | | | | | | | | | |
| HMC | 0.052 ± 0.004 | 5.28 ± 0.02 | 3.27 ± 0.02 | 1.38 ± 1.38 | 8.17 ± 0.11 | | | | | | | | | |
| COK | 0.022 ± 0.002 | 0.13 ± 0.01 | 3.58 ± 0.05 | 3.62 ± 0.34 | 0.05 ± 0.01 | | | | | | | | | |
| COT | 0.042 ± 0.002 | 0.24 ± 0.01 | 13.8 ± 0.35 | 3.71 ± 0.10 | 0.07 ± 0.01 | | | | | | | | | |
| MNM | 0.002 ± 0.001 | 0.27 ± 0.01 | 9.36 ± 0.43 | 0.41 ± 0.04 | 0.11 ± 0.01 | | | | | | | | | |
| MNK | 0.038 ± 0.002 | 0.20 ± 0.01 | 8.21 ± 0.20 | 0.55 ± 0.03 | 0.05 ± 0.01 | | | | | | | | | |

HRK: Carob coffee. HRM: Carob fruit. KNK: Gundelia coffee. KNM: Gundelia fruit. HMK. Date coffee. HMC: Date kernel. COK: Black cumin coffee. COT: Black cumin seed. MNK: Terebinth coffee. MNM: Terebinth fruit

processed foods were achieved and published. Most of the natural food products, herbs, spices, vegetables and fruits and wild edible plants have also been screened for their mineral compositions⁴⁻¹¹. As mentioned above, herbal coffees-thought to be as novel natural drinks and recently produced industrial scale-have not been studied for their chemical compositions. In the present study, mostly consumed five herbal coffees and their raw materials were screened for their mineral compositions.

EXPERIMENTAL

Herbal coffees and their raw materials: In this study, five different herbal coffees (black cumin coffee, carob coffee, date coffee, gundelia coffee and terebinth coffee) and their raw materials were obtained from local spice shops and markets in southeastern part of Turkey in 2011. Some distinctive characteristics of plant materials used for herbal coffee production are given in Table-1.

Chemical analysis pathway: Raw plant materials used for herbal coffee production were cleaned and washed by deionized water and air dried. Afterwards, these plant materials were demousturized at 70 °C for 48 h in an oven and ground for chemical analysis. And then 0.2 g samples of each plant and processed herbal coffee materials were put into burning cup and 5 mL HNO₃ 65 % (Merck, Darmastadt, Germany) and 2 mL H₂O₂ 30 % (Merck, Darmastadt, Germany) were added. Having incinerated in a HP-500 CEM MARS 5 microwave (crop. Mathews NC, USA) at 200 °C, the solution was cooled at room temperature for 45 min. Passes through a Wattman 42 filter paper and the filtrates, the extracts were cooled by high-deionized water in a 20 mL-polyethylene

bottles and kept at 4 °C in laboratory for ICP-AES analyses. All the analyses were made in triplicate.

Distilled deionized water was used in all analytical works. All the glassware and polyethylene bottles used in analyses were attentively leach with 2-4 % HCl and rinsed through deionized water for three times. R1 and R2 groups of Merck standards were used as analytical reagent grade chemicals. Standard solutions of Cd, Cu, Fe, Mn and Zn were prepared in 1 % HNO₃ immediately before the analysis by serial dilution of 1000 mg L⁻¹ stock solution stored in polyethylene bottles. Corn bran (standard reference material, 8433) and Peach leaves (standard reference material, 1547) were used as reference materials¹².

In the present study, determining of the minerals ICP-AES (Varian Vista-Pro, Australia) was used. The wave lengths of the method were Al (396,152), B (208,889), Ca (370,602), Cd (214,439), Co (230,786), Cr (205,560), Cu (324,754), Fe (238,204), K (404,721), Mg (383,829), Mn (257,610), Mo (203,846), Na (588,995), Ni (216,555), P (213,618), Pb (220,353), S (181,972) and Zn (213,857) in the extracts.

RESULTS AND DISCUSSION

According to the results (Tables 2-4) of chemical analysis, considerable variations among the herbal coffees and their raw materials in respect to mineral compositions are as follows. Totally 16 different minerals including heavy metals, macro and micro elements were detected in all the analyzed samples. Differences between the processed herbal coffees and their raw plant materials for the minerals were almost limited. But, considerable variations between some herbal coffees and their raw materials were also detected. In the present work, each

| TABLE -3 MINERAL COMPOSITIONS OF HERBAL COFFEES AND THEIR RAW MATERIALS | | | | | | | | | | | | | | |
|--|--------|----|-------|---|-----|-----|---|------|------|---|-----|------|---|-----|
| Materials | Ca | K | | | Na | | | | | S | | | | |
| HRK | 2859 ± | 77 | 10932 | ± | 271 | 149 | ± | 9,99 | 749 | ± | 32 | 593 | ± | 26 |
| HRM | 1858 ± | 50 | 9244 | ± | 47 | 39 | ± | 1,77 | 751 | ± | 21 | 536 | ± | 15 |
| KNK | 4822 ± | 70 | 7928 | ± | 141 | 44 | ± | 2,83 | 3498 | ± | 106 | 2010 | ± | 85 |
| KNM | 7365 ± | 25 | 18728 | ± | 156 | 49 | ± | 1,50 | 3142 | ± | 27 | 2606 | ± | 31 |
| HMK | 475 ± | 12 | 4149 | ± | 50 | 44 | ± | 3,08 | 1199 | ± | 15 | 943 | ± | 7 |
| HMC | 726 ± | 25 | 3438 | ± | 201 | 41 | ± | 3,02 | 606 | ± | 35 | 975 | ± | 20 |
| COK | 2365 ± | 50 | 10699 | ± | 513 | 30 | ± | 4,50 | 3916 | ± | 254 | 2276 | ± | 151 |
| COT | 5287 ± | 54 | 8596 | ± | 76 | 52 | ± | 2,51 | 5859 | ± | 50 | 2861 | ± | 78 |
| MNM | 1957 ± | 41 | 10656 | ± | 45 | 101 | ± | 3,51 | 2489 | ± | 35 | 1141 | ± | 30 |
| MNK | 2213 ± | 20 | 9742 | ± | 201 | 27 | ± | 2,01 | 1996 | ± | 76 | 1029 | ± | 25 |

HRK: Carob coffee, HRM: Carob fruit, KNK: Gundelia coffee, KNM: Gundelia fruit, HMK. Date coffee, HMC: Date kernel, COK: Black cumin coffee, COT: Black cumin seed, MNK: Terebinth coffee, MNM: Terebinth fruit

mineral group related each other are given in the Tables 2-4. The results of all the analyzed herbal coffees and their raw plant materials were discussed, separately.

Heavy metal concentrations of the analyzed herbal coffees and their raw materials are given in Table-2. Cadmium concentrations of the analyzed samples were very different. Interestingly, the highest and lowest cadmium values were determined in the date coffee and its kernel. The highest chrome and lead values were found in Gundelia fruits. Black cumin seeds had the highest copper and nickel contents (Table-2).

Variations among the plant samples in respect to heavy metals may be explained by their growing conditions, capturing capabilities from the soil and accumulation abilities of these minerals by the plants. In previous studies related to heavy metal concentrations of some food materials, different findings were published. In previous studies, cadmium concentrations in medicinal and aromatic plants were reported between 0.012 and 0.440 mg/kg^{6,7,10,13}. Our findings for cadmium in analyzed samples were much lower than that of cadmium acceptable limits for herbs and spices as 0.300 mg/kg by WHO¹⁴. According to related studies, the highest chromium concentrations of different medicinal and aromatic plants were 24.68 mg/kg in anise15, 2.40 mg/kg in Afat16, 4.18 mg/kg in Arnebia densiflora¹⁷. Kahvecioglu et al.¹⁸ reported that 0.030-0.200 mg daily chromium intake is sufficient for healthy life. Most of the coffees analyzed here had the acceptable chromium concentrations. Copper is very useful for humans, but excess intake of it may result some illnesses. Copper concentrations of some wild edible plants, cultivated vegetables and aromatic plants were found in the rates 0.05-23.3 mg/kg^{4,5,19,20}. Copper values found in this study are in harmony with the researchers' findings.

Nickel and lead concentrations of some wild edible plants in Turkey were found in the rates of 1.5-23.7 mg/kg and 0.04-1.40 mg/kg, respectively²¹. These two heavy metals are well-known hazardous for livings and commonly found in industrialized areas. Our findings for these two heavy metals are similar to researcher's results. According to all these reports, it could be stated that heavy metal concentrations of the herbal coffees and their plant raw materials analyzed in the present study were in the safe limits for human health.

Living organisms need some minerals in a certain quantities for their physiological activities and regularly maintain their life. Calcium, potassium, sodium, phosphorus and sulphur

are of these minerals. In this work, it was found that analyzed herbal coffee and plant materials had various contents of these minerals. As the highest calcium and potassium concentrations were determined in the Gundelia fruits and black cumin seeds had the highest phosphorus and sulphure contents (Table- 3). The highest sodium concentration was in the carob coffee samples. Considering each herbal coffee and their raw materials, it could be said that there were no considerable differences for mineral contents. Partial differences between the processed herbal coffee and raw materials could be explained by process techniques and methods.

In previous studies, similar results were reported by the scientists for food materials in respect to these minerals^{6,7,10,13}. Some minerals such as boron, iron, magnesium, manganese, molybdenum and zinc are useful for human in limited concentrations like in other organisms. Their deficiency may result serious health problems, as well. According to chemical analysis, it could be said that Gundelia fruits were a good source for boron and magnesium. Black cumin coffee was rich in manganese and molybdenum. As the Gundelia coffee had the highest iron contents, zinc concentration was the highest in black cumin seeds (Table-4).

According to recent scientific reports, wild edible plants are a good source such minerals^{6,21,22}. According to our results, herbal coffees could be considered as good sources for the mentioned minerals used in certain amounts.

Conclusion

This study is the first report indicating mineral compositions of herbal coffees and their raw materials. Determination of heavy metal concentrations and useful mineral content of food materials is very important for human health. According to instructions released by national authorities or international organizations, their acceptable concentrations for humans are very different. Among these reports, the most important ones are related to heavy metals. Their limits for foods and edible plants were almost determined by international organizations. In the present study, besides other minerals, we also discussed heavy metal concentrations of the traditional herbal coffees. According to results, it could be easily stated that heavy metal concentrations of the herbal coffees analyzed were in considerable levels. They also a good source for useful minerals, as well.

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| TABLE- 4 MINERAL COMPOSITIONS OF HERBAL COFFEES AND THEIR RAW MATERIALS | | | | | | | | | | | | | | | | | | | |
|---|-------|---|------|-----|---|------|------|---|----|----|------|---|------|------|---|------|------|---|------|
| Materials | | | Fe | | | Mg | | | | Mn | | | Mo | | | Zn | | | |
| HRK | 11.50 | ± | 0.40 | 18 | ± | 0.41 | 659 | ± | 41 | | 4.9 | ± | 0.18 | 0.08 | ₹ | 0.01 | 7.5 | ± | 0.35 |
| HRM | 8.92 | ± | 0.20 | 47 | ± | 1.00 | 482 | ± | 5 | | 3.8 | ± | 0.18 | 0.13 | Ⅎ | 0.02 | 5.0 | ± | 0.04 |
| KNK | 12.58 | ± | 0.71 | 145 | ± | 5.65 | 2031 | ± | 77 | | 18.5 | ± | 2.12 | 1.05 | ₫ | 0.07 | 19.6 | ₹ | 0.57 |
| KNM | 28.03 | ± | 2.00 | 134 | ± | 2.67 | 2481 | ± | 15 | | 11.1 | ± | 0.26 | 0.72 | ₹ | 0.03 | 14.4 | ± | 0.31 |
| HMK | 5.17 | ± | 0.18 | 24 | ± | 1.57 | 787 | ± | 7 | | 10.8 | ± | 0.75 | 0.04 | ₹ | 0.01 | 12.8 | ₹ | 0.25 |
| HMC | 6.16 | ± | 0.35 | 39 | ± | 3.03 | 720 | ± | 35 | | 13.8 | ± | 1.25 | 0.01 | Ⅎ | 0.01 | 12.8 | ₫ | 0.53 |
| COK | 12.78 | ± | 0.53 | 106 | ± | 5.11 | 1736 | ± | 40 | | 30.4 | ± | 3.73 | 1.97 | Ⅎ | 0.10 | 35.7 | ₫ | 3.03 |
| COT | 24.81 | ± | 2.05 | 83 | ± | 2.03 | 2375 | ± | 52 | | 26.2 | ± | 1.11 | 0.43 | Ⅎ | 0.02 | 54.1 | ₫ | 2.07 |
| MNM | 13.81 | ± | 0.66 | 80 | ± | 3.83 | 915 | ± | 25 | | 8.9 | ± | 0.35 | 0.02 | Ⅎ | 0.01 | 13.3 | ₫ | 0.65 |
| MNK | 13.78 | ± | 0.61 | 45 | ± | 1.58 | 727 | ± | 20 | | 6.7 | ± | 0.20 | 0.01 | ₫ | 0.01 | 9.8 | ± | 0.16 |

HRK: Carob coffee. HRM: Carob fruit. KNK: Gundelia coffee. KNM: Gundelia fruit. HMK. Date coffee. HMC: Date kernel.

COK: Black cumin coffee. COT: Black cumin seed. MNK: Terebinth coffee. MNM: Terebinth fruit

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