ARAŞTIRMA MAKALESİ / RESEARCH ARTICLE

DANDELION HONEY: A NEW MONOFLORAL HONEY RECORD FOR TURKEY

Karahindiba Balı: Türkiye Monofloral Balları İçin Yeni Bir Kayıt

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ABSTRACT

Taracaxum **species are an important food source for many insects because of their early flowering and rich supply of nectar and pollen.** ***Taraxacum*** **(dandelion) honey has been characterized and is wide-spread throughout Europe. Although, Turkey, Iran, Afghanistan and the West Himalayas have the highest species richness and character diversities of** ***Taraxacum*****, there are still gaps of knowledge about dandelion honey. The aim of this study was to evaluate the composition of dandelion honey which will be a new characterization of a monofloral honey originating from Turkey.**

Key words: *Taraxacum,* Dandelion, Honey, Turkey

ÖZ

Taracaxum **türleri erken çiçeklenme dönemleri sebebiyle pek çok böcek için önemli bir polen ve nektar kaynağıdır.** ***Taracaxum*** **(karahindiba) balı Avrupa'da üretilmekte olan ve karakterizasyonu yapılmış bir baldır. Türkiye, İran, Afganistan ve Batı Himalayalar** ***Taraxacum*****, tür zenginliği ve karakter çeşitliliği açısından en önemli bölgelerdir. Ancak bu bölgelerde karahindiba balı ile ilgili ciddi boşluklar bulunmaktadır. Bu çalışmanın amacı Türkiye monofloral balları açısından yeni bir kayıt olan karahindiba balının melissopalinolojik ve kimyasal içeriğinin değerlendirilmesidir**.

Anahtar kelimeler: Taraxacum, Dandelion, Bal, Türkiye

GENİŞLETİLMİŞ ÖZET

Taraxacum türleri erken çiçeklenme dönemleri sebebiyle pek çok böcek için önemli bir polen ve nektar kaynağıdır. *Taracaxum* (karahindiba) balı Avrupa'da üretilmekte olan ve karakterizasyonu yapılmış bir baldır. Türkiye, İran, Afganistan ve Batı Himalayalar *Taraxacum*, tür zenginliği ve karakter çeşitliliği açısından en önemli bölgelerdir. Ancak bu bölgelerde karahindiba balı ile ilgili ciddi boşluklar bulunmaktadır. Bu çalışmanın amacı Türkiye monofloral balları açısından yeni bir kayıt olan karahindiba balı için melissopalinolojik ve kimyasal içerik analizlerinin yapılmasıdır.

Karahindiba balı, Bingöl ili sınırları içerisinde arıcılık yapmakta olan arıcıların laboratuvarımıza analiz için gönderilen ballar içerisinden tespit edilmiştir. Dominant polen %96 oranı ile karahindiba kökenlidir. Kimyasal

analizler: nem içeriği, GC-MS ile uçucu kimyasal bileşenlerin tespiti, HPLC ile glikoz ve früktoz şeker içeriklerinin tespiti, HPLC ile HMF içeriğinin tespiti ve UV-spektrofotometre ile fenolik içeriğinin saptanmasıdır.

Nem içeriği %14.9 olarak tespit edilmiştir. Karahindiba balının GC-MS ile yapılan uçucu bileşen analizine göre alkoller, aldehitler, yağ asitleri ve bunların esterleri, amino asitler, karboksilik asitler, aminler, aromatik amitler ve diğer kimyasal bileşikler ortaya çıkarılmıştır.

% 11.71 gliseraldehid ve% 8.62 benzamid, 2,4,6-trinitro-N, N-dimetil-bileşiği içerdiği gözlenmiştir. Gliseraldehit diğer bileşiklerle karşılaştırıldığında en yüksek oranda bulunur. "Butanal, 3 metil" oldukça yüksek bir oranda (%7.89) bulunmuştur.

Früktoz % 46.02, glükoz % 35.21 ve früktoz / glükoz oranı 1.3 olarak bulunmuştur. HMF değerini 1.73 ppm, toplam fenolik içeriği 38.93 ± 0.49mg GAE / 100g olarak bulunmuştur.

Ülkemizde üretilebilecek karahindiba balının karakterizasyonu için daha çok sayıda örnekle çalışılmalıdır. Bal üreticisi ve tüketicisi ile ekonomik açıdan da değerlendirmeler yapılarak, Türkiye'de üretilmekte olan monofloral ballara bir yenisinin eklenebileceği düşünülmektedir.

INTRODUCTION

The genus *Taraxacum* is a member of the family Asteraceae, subfamily Cichorioideae, tribe Lactuceae and is found widely distributed in the warmer temperate zones of the Northern Hemisphere, inhabiting fields, roadsides and rural sites (Schütz et al., 2006). According to Richards (1973) the most ancestral forms of this genus are centered in west and central Asia. The highest species and character diversities are found in Turkey, Iran, Afghanistan and the West Himalayas, but a similar richness is encountered also in north-central China and the southern Caucasus (Gurdal et al., 2017). In Turkey, the genus is represented by at least 62 taxa, 18 of them are endemic to the country (Gurdal et al., 2017).

Due to its early flowering and rich supply of nectar, in Canada *T. officinale* is an important food source for many insects, including butterflies, bees flies, hawk moths and bumble bees (Jackson, 1982; Stewart-Wade et al., 2002). More than 140 different non-specialist insect pollinators have been recorded on *Taraxacum* flowers. Besides pollen, the inflorescences provide nectar for pollinators. The single seeded fruits (achenes) are plumed with pappus and are effectively transported by wind (Van Dijk, 2007).

In Europe more than 100 botanical species are known to produce unifloral honey (Oddo et al., 2004). Most of them are produced occasionally or are only of local interest, whereas others are part of the import-export market between different European countries (Oddo et al., 2004).

According to the International Honey Commission, *Taraxacum* pollen rarely exceeds 50% in *Taraxacum* labelled honeys, the contributions of other associated plants, such as from *Salix* or Brassicaceae, are found higher proportions (Oddo et al., 2004, Soria et al., 2008).

Taraxacum honey has been also characterized with melissopalynology, physicochemical and sensory characteristics (Oddo et al., 2004). Although Turkey, Iran, Afghanistan and the West Himalayas have the highest species richness and character diversities of *Taraxacum*, there is not any data about the dandelion honey originating from these regions.

The aim of our study is to evaluate a new unifloral honey produced from Turkey: dandelion honey. This will be the first characterization of dandelion honey originating from Turkey.

MATERIALS AND METHODS

Melissopalynological analysis

Honey samples were sent to our laboratory from the Bingöl province in the summer season of 2017. The samples were stored at 22 ± 2°C until the time of analyses.

The materials were prepared for examination under the microscope according to the method of Louveaux et al. (1970) and Sorkun (2008).

Observed pollen types were classified into three categories: dominant pollen (≥ 45%, D), secondary pollen (16–44%, S), important minor pollen (>3–15%, M) and rare pollen (3%<). When one pollen type represented >45% of the total number of pollen grains, the sample was classified as a monofloral honey (Louveaux et al., 1978).

Moisture

A portable refractometer was used to determine the moisture content of the honey (Bogdanov, 1997, Devillers et al., 2004).

Gas chromatography-mass spectrometry (GC-MS) analysis

The Method for GC-MS was performed in accordance with Barcarola et al, (1998), Radovic et al.,(2001), Soria et al.,(2003), and Cuevas-Glory et al.,(2007).

A GC 6890N from Agilent (Palo Alto, CA, USA) coupled with mass detector (MS5973, Hewlett-Packard) was used for the analysis of EEP samples. Experimental conditions of the GC-MS system were as follows: a DB 5 MS column (30 m x 0.25 mm and 0.25 µm of film thickness) was used with a flow rate of mobile phase (He) that was set at 0.7 mL/min. In the gas chromatography part, the temperature was kept at 50°C for 1 min. After this period, the temperature was increased to 150°C with a 10°C/min heating ramp and then kept at 150°C for 2 min. Finally, temperature was increased to 280°C with a 20°C/min heating ramp and then kept at 280°C for 30 min. Chemical components were identified by using standard Willey and Nist Libraries available in the data acquisition system of GC–MS if the comparison scores were obtained higher than 90%.

Sugar analysis by high-performance liquid chromatography (HPLC)

Sugar analyses (fructose and glucose) were performed according to the harmonized methods of the International Honey Commission (Bogdanov et al., 2002). In a 100-mL volumetric flask 5 g of honey was dissolved in 40 mL water. The honey solution was mixed with 25 mL of methanol. The flask was filled up to with water. The solution was poured through a 0.45 µm membrane filter and collected in sample vials.

The analyses conducted by HPLC (Agilent Technologies 1200 Series, Germany) with a refractive index detector (HPLC-RID) using a carbohydrate column (Agilent Technologies Carbonhydrate 5 µm, 4, 6 x 250 mm, USA).

Determination of hydroxyl methyl furfural (HMF) by High Performance Liquid Chromatography (HPLC)

HMF content was determined according to the harmonised methods of international honey commission's suggestions (Bogdanov et al., 2002). 10 g of honey was dissolved with 25 mL of water. The solution was diluted with 50 mL water and then filtered through a 0.45 µm membrane filter. The samples were analyzed by HPLC (Agilent Technologies, USA) with a UV detector (Agilent Technologies, USA) and a C-18 reversed phase column (Agilent Technologies, USA).

Determination of total phenolic contents by UV

Total phenolic contents of samples were analysed by the Folin & Ciocalteu's phenol reagent (Folin C) colorimetric method described by Slinkard & Singleton (Slinkard and Singleton, 1977).

RESULTS

Plant taxa determined by melissopalynological analysis

As a result of the melissopalinological analysis, it was determined that *Taraxacum* spp. pollen was dominant with 96% prevelance. The rare pollen composition of the honey was determined to be *Carduus* spp. (2.4%), Fabaceae (0.96%) and Euphorbiaceae (0.5%). The total amount of pollen in honey was found to be 7786.

Moisture

The moisture content of dandelion honey was determined as 14.9%.

Gas chromatography-mass spectrometry (GC-MS) analysis

GC-MS chemical compounds analysis of dandelion honey revealed alcohols, aldehydes, fatty acids and their esters, amino acids, carboxylic acids, amines, aromatic amides and other chemical compounds.

Table 1. Chemical compositions of dandelion honey sample
Tablo 1. Karahindiba balının kimyasal kompozisyonu

Compounds	Taraxacum Honey
Alcohols	
Benzenemethanol, .alpha.-(1-aminoethyl)-, [R-(R*,S*)]- (CAS) NOREPHEDRINE	0,03
Ethanol, 2-bromo- (CAS) 2-Bromo	1,78
Ethanol, 2-bromo-(CAS) 2-Bromoethanol Ethylene bromohydrin	8,83
1,2-Ethanediol, diformate (CAS) ETHYLENE DIFORMATE Glycol diformate	0,23
Aldehydes	
Glyceraldehyde	11,71
Pentanal (CAS)	3,26
Butanal, 3-methyl-	7,89
Fatty Acids and Their Esters	
Octadecanoic acid (CAS)	0,08
Amino acids	
L-Alanine, ethyl ester	0,27
Carboxylic acids	
1-Piperazinecarboxylic acid (CAS) PIPERAZINE CARBONATE	1,14
Acetic acid, hydroxy[(1-oxo-2-propenyl)amino]-2-Acrylamidoglycolic acid	3,00
Amines	
1-Propanamine, N,2-dimethyl- Propylamine, N,2-dimethyl-	0,49
n-Hexylmethylamine N-n-Hexylmethylamine 1-Hexanamine, N-methyl	1,05
1-Pentanamine, N-methyl- $$ Pentylamine, N-methyl- Methylamylamin	0,69
2-Butanamine, 3-methyl- (CAS) 2-Amino-3-methylbutane	0,10
1-Methyldodecylamine 2-Aminotridecane	0,56
Aromatic amides	
Benzamide, 2,4,6-trinitro-N,N-dimethyl-	8,62
1,2-Hydrazinedicarboxamide Biurea Hydrazodicarbonamide	0,69
Urea, N-methyl-N-nitroso- (CAS) N-Nitroso-N-methylurea NSC 23909	1,41
Others	
Piperazine (CAS) R22 Uvilon Antiren Pipersol Lumbrica	1,76
1,2,4-Triazine aS-Triazine	2,86
(tetrahydroxycyclopentadienone)tricarbonyliron(0)	4,35
4H,6H-Thieno[3,4-c]furan/	3,81
Propanenitrile, 3-(methylamino)-	0,06
2,4(1H,3H)-Pyrimidinedione, 5-nitro- 5-Nitrouracil	0,08

Sugar analysis by high-performance liquid chromatography (HPLC)

Sugar content of dandelion honey was determined as 46.02% fructose, 35.21% glucose, and a ratio of 1.3 of fructose to glucose.

Determination of hydroxyl methyl furfural (HMF) by High Performance Liquid Chromatography (HPLC)

We found the HMF value to be 1.73 ppm.

Determination of total phenolic contents by UV

The total phenolic content of *Taraxacum* honey was found to be 38.93± 0.49mg GAE/100g.

DISCUSSION

Italian *Taraxacum* honey is characterized by low percentages (usually 5 to 15%) and a relatively high absolute pollen content, because of its almost constant contamination with *Salix* (which is over-represented) (Oddo et al., 1995). The dandeilon honey originating from Turkey, had 96 % of pollen composition classified as *Taraxacum* spp., making it a monofloral honey.

Quick complete granulation with fine regular crystals, a cream to yellow color, with sometimes a greyish hue, and an intense pungent ammoniacal persistent smell and flavor, are the other typical features of Italian dandelion honey (Oddo et al., 1995).

Water content (%) was found to be 16.9 ± 0.9 (n = 23) (Oddo et al., 1995). According to our results, the moisture content of dandelion honey was determined to be 14.9%. The difference observed can be attributed to the harvest time or the weather conditions.

Throughout the ages, several health-promoting benefits, including diuretic, laxative, cholagogue, anti-rheumatic, antiinflammatory, choleretic, anti-carcinogenic and hypoglycemic activities, have been attributed to the use of dandelion extracts or the plant itself (Schütz et al., 2006). GC-MS chemical compounds analysis of dandelion honey revealed alcohols, aldehydes, fatty acids and their esters, amino acids, carboxylic acids, amines, aromatic amides and other chemical compounds.

Soria et al. (2008) identified some kind of nitrile compounds in honey that is labelled as *Taraxacum* honey. Similar to their results we found a nitrile compound "Propanenitrile, 3-(methylamino)" at 0.06%, but the authors also mention that the nectar contribution of species belonging to the Brassicaceae family is likely the origin of the relatively high amounts of nitriles in *Taraxacum* honey.

According to the volatile component analysis by GC-MS, we were observed that dandelion honey contains 11.71% glyceraldehyde and 8.62% benzamide, and the 2, 4, 6-trinitro-N,N-dimethyl compound. Glyceraldehyde is found in the highest percentage compared to the other compounds. Owing to the literature, there is no data about this compound found in any kind of honey. Another compound "Butanal,3 methyl" is found with at a quite high percentage (7.89%) compared to the other determined volatile compounds. It is also not found in the composition of any other honey samples to our knoledge. These three compounds (Glyceraldehyde, benzamide, 2, 4, 6-trinitro-N,N-dimethyl, Butanal, 3 -methyl) can therefore be considered as biomarker compounds for *Taraxacum* honey, but further research is needed to validate these biomarkers. Octadecanoic acid, also called Stearic acid, is one of the linear fatty acid esters and it is nature's most common long-chain fatty acids, derived from animal and vegetable fats. It is widely used as a lubricant and as an additive in industrial preparations. It is used in the manufacture of metallic stearates, pharmaceuticals, soaps, cosmetics, and food packaging (Özkök et al. 2016). This compound was found in low concentrations in the dandelion honey. Further research is necessary to fully chemically characterize *Taraxacum* honey.

Sugar content of Italian dandelion honey were determined as 38.8 ± 1.9% fructose, 39.1 ± 2.5% glucose, having a ratio 0.99 ± 0.05 of fructose to glucose, and 1.2 ± 1.5% sucrose (n = 14) (Oddo et al., 1995). We found 46.02% fructose, 35.21% glucose and a 1.3 fructose/glucose ratio.

Both *Helianthus* and *Taraxacum* honey have very high monosaccharide (particularly glucose) content, giving rise to a very high G/W and a very low F/G ratio. This is typical for honey which granulates rapidly (Oddo et al., 1995).

The European Union (EU Directive 110/2001) established that the highest allowed amount of HMF in honey should be 40 ppm, with the exception of honey from tropical origin (80 ppm). Our obtained results were all lower than legal limits with 1.73 ppm and an HMF of 3.5 ± 3.7 mg/kg (n = 23) (Oddo et al., 1995).

Habati et al. (2017) found the total phenolic content of *Zizyphus lotus* honey as 38 mgGAE/100g. Sime et al., (2015) investigated the total phenolic contents of 10 multifloral honey samples and found the values between 330 - 610 mgGAE/100g. Rababah et al. (2012) investigated 12 multifloral honey samples and found the total phenolic values between 33.7 ± 1.2 and 86.3 ± 2.7 mg GAE/100g. Krpan et al. (2009) studied 30 Acacia honey samples and found their total phenolic contents ranging from 31.72 mg/kg to 80.11 mg/kg.

Pontis et al (2014) analyzed 10 honey samples from Roraima, Brazil, and found the total phenolic contents of these honey samples to be between 250 ± 3.24 and 548 ± 3 mg/kg. Meda et al. (2005) found the total phenolic contents of bretaceae honey as 52.08 ± 0.31 and 59.67 ± 1.35 mg GAE/100g, Acacia honey as 93.43 ± 0.87 mg GAE/100g, honeydew honey as 113.05 ± 1.3 and 114.75 ± 1.30 mg GAE/100g, Vitellaria honey as 76.10 ± 0.56 and 83.53 ± 0.25 mg GAE/100g, respectively. Our results show similarities with *Zizyphus lotus* honey and compared to the other honey types it has lower total phenolic content.

CONCLUSION

Palynological and chemical compositions are the two important characters to classify the honey. Marketing of honey is only possible if these features have been evaluated. Honey is marketed specifying its botanical and geographical origin on the label, in order to guarantee authenticity and quality (Escriche et al., 2017).

Although *Taraxacum* honey is a new characterization record for Turkey honey, it has been characterized by International Honey Commission nearly three decades ago. Dandelion honey is a very traditional honey type in Austria. In Turkey, *Taraxacum* species are a really important nectar and pollen source for beekeepers due to its early flowering and rich supply of nectar, but beekeepers are not harvesting this kind of honey separately. Further investigations are necessary for the characterization of *Taraxacum* honey produced in Turkey. In our opinion, this value should be recognized by researchers and beekeeping industry.

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