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RESEARCH ARTICLE

Chemical composition of the essential oil of sea fennel seed (*Crithmum maritimum* L.) from Turkey

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Abstract

This study was carried out to determine the essential oil composition of the sea fennel, *Crithmum maritimum* seed collected from Arsuz, Hatay (Turkey). The components of the essential oil were identified through GC/MS. The identity of 23 compounds of the essential oil was confirmed and their relative proportion was determined. The yield of essential oil was found 0.6%. Monoterpenic hydrocarbons: sabinene (43.29%), p-cymene (13.27%), α-phellandrene (13.16%), α-pinene (10.58%) and γ-terpinene (10.56%) were major compounds in essential oil of sea fennel seed. Sabinene has the highest percentage composition in the *C. maritimum* seed essential oil (43.29%). It is suggested that the sea fennel seed can be used as a trading source for commercial cultivation and potential medicinal uses of *C.maritimum* in Turkey.

Keywords: Sea fennel, *Crithmum maritimum*, essential oils, GC/MS

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Introduction

Sea fennel (*Crithmum maritimum* L.), the only species of the genus *Crithmum*, is an aromatic herb belonging to the Apiaceae family (Pistrick 2002). Sea fennel (*Crithmum maritimum* L.) is a halophytic plant that grows wild on maritime rocks, piers, and breakwaters, more rarely on sandy beaches along the Mediterranean countries, Pacific and Atlantic coasts. It grows on the coasts of all round the world, but is especially abundant in the coastal regions of France, Italy, Portugal, Spain and Turkey (Davis and Tan 1988; Coiffard *et al.* 1993;

Senatore and De Feo 1994). *C. maritimum* is a highly branched plant of up to 30–60 cm high with a strong, thick and gnarled root. Leaves are succulent and have a sheath like base with the short petiole ending in a pinnate composed blade, which is usually divided into three leaflets 25 cm long. The plant blooms between June and September, while the fruit begins to ripen in November-December (Atia *et al.* 2011).

In many countries, sea fennel is traditionally used in cuisine as a fresh ingredient due to its interesting sensory attributes (Renna and Gonnella 2012), owing to its richness in essential oils (Pateira *et al.* 1999; Ozcan *et al.* 2001). The fresh leaves can be used for salads, soups and sauces, or they are kept like capers in vinegar (Renna *et al.* 2017). Its seeds contain also appreciable amounts of edible oil, rich in essential fatty acids (Zarrouk *et al.* 2004). In former times sea fennel leaves were used in folk medicine as antiscorbutic, tonic, carminative, diuretic, depurative and vermifuge. Sailors were used to eating fresh leaves as protection against scurvy during fishing trips (Baytop 1984; Senatore *et al.* 2000; Ozcan *et al.* 2001; Atia *et al.* 2011). The essential oils of sea fennel are also widely used in cosmetics (Atia *et al.* 2011; Jallali *et al.* 2014).

Although in the case of sea fennel usually leaves are used, other plant parts which remain unused could also be useful for culinary or medicinal purposes. Due to the possible different chemical composition and their yield in different plant parts (Pateira *et al.* 1999; Houta *et al.* 2011), it is important to investigate them separately in order to understand their biological potential. The majority of studies on sea fennel in Turkey investigated the qualitative and quantitative composition of its essential oils from Turkey (Senatore *et al.* 2000; Ozcan *et al.* 2001, 2006; Akyurt and Erikli 2016), Portugal (Pateira *et al.* 1999), Italy (Ruberto *et al.* 2000), to support the hypothesis that several different chemotypes of sea fennel grow in the Mediterranean region. They reported significant fluctuations in essential oil composition containing monoterpenes as the main compounds, while studies on sea fennel chemistry, especially on its polar components and their biological activities are scarce (Meot-Duros and Magne 2009). There is, however, a lack of information in the literature regarding chemical composition of the essential oils of sea fennel seed from different regions of Turkey. Therefore, the aim of this paper is to determine the essential oils composition of the seed of *C. maritimum* collected from Arsuz, Hatay region of Turkey by using Gas Chromatography - Mass Spectrometry (GC/MS) and provide the users and investigators with more precise data.

Materials and Methods

Plant material

Samples of *Crithmum maritimum* were randomly collected along the shoreline near Arsuz, Hatay, (36˚24' 15.2"N; 35˚52' 19.0"E) Turkey in April-May, 2019 (Figure 1).

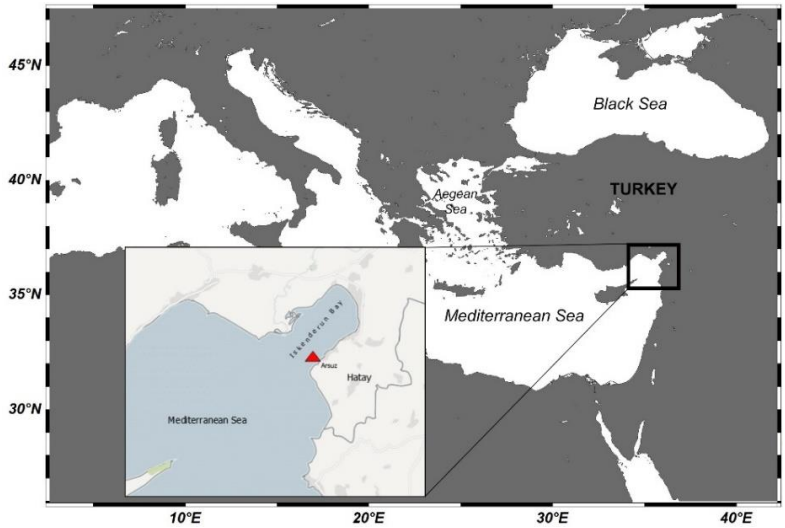

Figure 1. Map of sampling site (▲) in Hatay, Turkey.

The samples were transferred to the laboratory and, after removing any inedible parts, was washed with tap water and blotted dry with paper towels. The samples were identified and deposited in the Department of Marine Science and Technology, Iskenderun Technical University (Figure 2).

Figure 2. Fresh samples of sea fennel (*Crithmum maritimum*)

Isolation of the essential oils

To extract the essential oil, 50 gram of air-dried seeds were subjected to water distillation for 3 h using a Clevenger-type apparatus. The oil was dried over anhydrous $CaCl_2$ and stored in sealed vials in refrigerator (4℃) before analysis. The essential oil yield was estimated by the following equation (Boutekedjiret *et al.* 2003).

$$RHE\ (\%) = (mHE/mS) \times 100$$

mHE : essential oil mass (g),
mS : dry plant matter mass (g),
RHE: essential oil yield (%).

The yield of essential oil was calculated by mL/100g seeds and the yield was found 0.6%.

Analysis and identification of components

The essential oil was analysed by GC/MS using a Finnigan-Trace GC/MS equipped with an auto sampler, Zebron ZB-5 capillary column (5 % phenyl-95% dimethylpolysiloxane, 0.25 mm i.d.x 60m, film thickness 0.25 µm). One microliter of sample volume was injected using split method with 50 split ratio. Analysis was carried out using helium as the carrier gas with the flow rate 1.0 mL/min. The chromatogram was produced by holding the oven temperature to 50 ℃ for 5 min initially, increasing to 150 ℃ at rate of 3 ℃/min, followed by an increase at a rate of 5 ℃/min then kept constant at 280 ℃ for 5 min. The sample size was 1.5 mL. The injection port temperature was 250 ℃. The ionization voltage applied was 70 eV, mass range m/z 41-400 a.m.u. The separated components were identified tentatively by matching with GC/MS results of National Institute of Standards and Technology (NIST), Wiley Library, WILEY275, NBS75K, FLAVOR mass spectral libraries data because their reference reagents were available. The quantitative determination was carried out based on peak area integration.

Results

Essential oil constituents of sea fennel seeds are listed in Table 1 in order of their retention indices. Overall, 23 compounds representing 100% of the seed oil were identified. GC/MS analysis of essential oil in wild-grown sea fennel seeds showed that monoterpenic hydrocarbons: sabinene (43.29%), p-cymene (13.27%), α-phellandrene (13.16%), α-pinene (10.58%) and γ-terpinene (10.56%) were major compounds. Monoterpenic hydrocarbons were found predominantly in the seed oil and sabinene had the highest composition (43.29%) in the *C. maritimum* seed essential oil (Table 1, Figure 3).

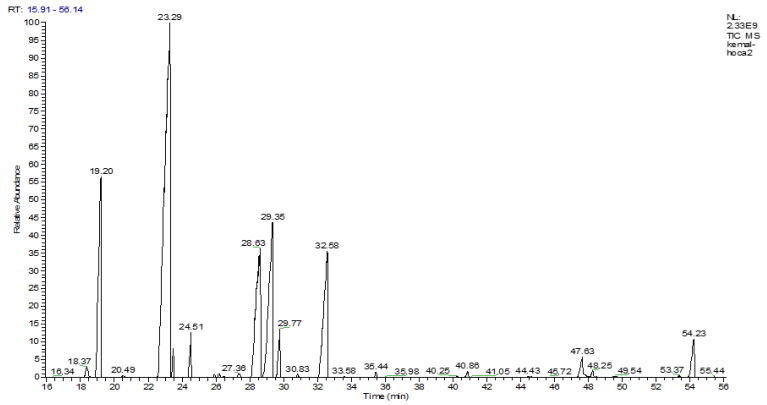

Figure 3. GC/MS chromatographic profile of the essential oil in *Crithmum maritimum* seed

Table 1. Relative contents of essential oil composition in *Crithmum maritimum* seed collected from Arsuz, Hatay (Turkey)

RT*	Compounds	Relative contents (%)
18.37	3-thujene	0.55
19.2	α-pinene	10.58
20.49	camphene	0.07
23.29	sabinene	43.29
23.47	2-α-pinene	0.58
24.51	α-myrcene	1.47
25.91	pseudolimonene	0.08
26.18	l-phellandrene	0.12
26.46	δ-3-carene	0.04
27.36	α-terpinene	0.17
28.63	p-cymene	13.27
29.35	α-phellandrene	13.16
29.77	cis-ocimene	1.91
30.83	trans-ocimene	0.09
32.58	γ-terpinene	10.56
33.58	trans-sabinene hydrate	0.02
35.44	terpinolene	0.18
40.86	alloocimene	0.2
47.63	4-terpineol	1.22
48.25	cryptone	0.24
49.54	p-menth-3-en-7-al	0.04
53.38	carvacrol methyl ether	0.06
54.23	thymol methyl ether	2.1

*RT = Retention Time

Discussion

After the isolation of essential oil from sea fennel seed, sabinene (43.29%), p-cymene (13.27%), α-phellandrene (13.16%) were identified as major

components. This is the first report of sea fennel seed essential oil from Arsuz, Hatay (Turkey). The essential oil compositions of sea fennel collected from various regions of Turkey have been reported (Baser *et al.* 2000; Senatore *et al.* 2000; Ozcan *et al.* 2001, 2006; Akyurt and Erikli 2016). Senatore *et al.* (2000) reported that α-phellandrene and thymol methyl ether were identified as major compounds in sea fennel leaves and stem essential oil from Antalya (Turkey), while γ-terpinene and dill-apiole were identified as dominant in essential oil from Mersin (Turkey). Ozcan *et al.* (2001) reported that the samples were classified into groups according to the main components: sabinene, c-terpiene, methyl thymol and terpinen-4-ol; c-terpinene, dill apiol and sabinene; c-terpiene, methyl thymol and limonene; p-cymene, methyl thymol and c-terpinene. (Z)-b-ocimene.

There are also many reports of the composition of essential oils obtained from sea fennel grown in other parts of the Mediterranean Sea coast. Results from these studies showed that the chemical constituents of essential oil of sea fennel may vary with locality. Pateira *et al.* (1999) reported that the major oil components in sea fennel from Portugal were dillapiol, sabinene, γ-terpinene and thymol methyl ether. Ruberto *et al.* (2000) reported that essential oil of sea fennel from Sicily constituted mostly of limonene, γ-terpinene and thymol methyl ether as main components.

According to these studies, it can be concluded that components that can be found as major constituents in the oil of sea fennel are monoterpenes. The identified constituents are in agreement also with the composition of the essential oils reported in Ozcan *et al.* (2006), even if many reports on the essential oil composition of sea fennel grown in different parts of the Mediterranean coast showed differences in chemical constituents, suggesting different chemotypes of this species (Kulisic-Bilusic *et al.* 2010).

According to our results, the major compound found in the seed oil from plants collected along Arsuz, Hatay (Turkey) was sabinene (43.29%). Monoterpenes were the most abundant compounds in the seeds, with 1,8-cineole and sabinene as the main compounds. There are reports that, monoterpene hydrocarbons (sabinene, α-terpinene) and oxygenated monoterpenes (1,8-cineole, α-terpinenol, terpinen-4-ol) have shown antioxidant activity (Ruberto and Barata 2000; Ozcan *et al.* 2010). Moreover, Kazemi (2015) reported that *Anethum graveolens* essential oil and its main compounds (limonene (45%) and sabinene (32%)) revealed antioxidant and anti-inflammatory effects and these results support the traditional use of this plant in antimicrobial activity, relieving pain and inflammation. Quiroga *et al.* (2015) noticed that the essential oils rich in thymol and sabinene hydrate showed high antioxidant activity and could possibly replace synthetic antioxidants such as butylated hydroxy anisole (BHT) in other similar food products even though they had lower antioxidant activity.

Consequently, the essential oil of *C.maritimum* seed and its main compound, sabinene (43.29%), can be used as an effective antioxidant and anti-inflammatory compound. Our study provides useful information for commercial cultivation and potential medicinal uses of *C. maritimum* in Turkey. Seeds, especially the unripe ones, were the best part for attaining a maximum yield of essential oil. When the plant was used as food and herbal medicine, the importance of careful selection of plant parts with higher phytochemical and biological activities would be revealed (Ebadi *et al.* 2019). These properties can imply the potential for use of sea fennel seed oil in pharmaceutical and other industries.

Türkiye'de bulunan deniz rezenesi (*Crithmum maritimum* L.) tohumunun esansiyel yağının kimyasal bileşimi

Öz

Bu çalışma, Hatay'ın Arsuz sahillerinden (Türkiye) toplanan Deniz rezenesi (*Crithmum maritimum*) tohumunun esansiyel yağ bileşimini belirlemek amacıyla yapıldı. Esansiyel yağın bileşenleri GC/MS ile tanımlandı. Esansiyel yağın 23 (yirmi üç) bileşiği ve nispi oranı belirlendi. Uçucu yağ verimi % 0.6 olarak bulundu. Monoterpenik hidrokarbonlardan: sabinen (% 43.29), p-cymene (% 13.27), α-phellandrene (% 13.16), α-pinen (% 10.58) ve γ-terpinen (% 10.56) deniz rezene tohumunun esansiyel yağındaki ana bileşiklerdir. Sabinene, *C. maritimum* tohumunun esansiyel yağında (% 43.29) en yüksek yüzde bileşimine sahiptir. Sonuç olarak; Deniz rezenesinin, Türkiye'deki potansiyel tıbbi kullanımları için bir ticaret kaynağı olarak kullanılabileceği önerilmektedir.

Anahtar kelimeler: Deniz rezenesi, *Crithmum maritimum*, esansiyel yağ, GC/MS

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