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Original Article

Chemical Composition Essential Oils of *Bunium kuhitangi* Nevski and *Bunium microcarpum* (Boiss) Freyn & Bornm.

Mohammad Baghr Rezaee, Kamkar Jaimand*, Razeeh Azimi, Mahmmod Nadery, Somieh Fekry and Mostafa Golypour

Research Institute of Forests and Rangeland, Agricultural Research, Education and Extension Organization (AREEO) Tehran, Iran

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Abstract

The genus *Bunium* (Apiaceae) comprises about 50 species spreading in Asia, Europe and North Africa. The genus *Bunium* comprised 14 species in Iran. It has various biological activities related to digestive and urinary tract disorders. In traditional medicine, it has been used in chronic stomach diseases, colitis, jaundice, chronic cholangitis, swelling and kidney stones. Aerial parts of *Bunium kuhitangi* Nevski and *Bunium microcarpum* (Boiss) Freyn & Bornm. were collected from Golestan provience, Gorgan, Golestan Park, on June 2020, essential oil extracted by water distillation method (Clevenger-type apparatus) for 3 h to obtain the essential oil. Chemical composition of the essential oil was analyzed by Gas chromatography (GC), Gas chromatography and Mass spectrometry (GC-MS), simultaneously. Main components from *B. kuhitangi* . were 9-epi-(E)- caryophyllene (35.38%), α- copaene (8.38%) and δ- selinene (7.35%) and main components for *B. microcarpum*. were 9-epi-(E)- caryophyllene (73.61%), γ- cuprenene (8.37%) and α-cadinene (5.75%). β-caryophyllene is a pale yellow oily liquid with an odor midway between odor of cloves and turpentine. To the best of our knowledge, this is the first report on the chemical constituents of *B. kuhitangi*. from Iran. In this study, it was aimed to clarify the chemical profile of essential oil obtained from *B. kuhitangi* and *B. microcarpum*. and to determine its main compounds.

Keywords: Apiaceae, *Bunium kuhitangi* Nevski and *Bunium microcarpum* (Boiss) Freyn & Bornm., Essential oil, Chemical composition

Introduction

The genus *Bunium* is represented in the flora of Iran by 14 species including two endemics. These are *B. lurestanicum* Rech. f. and *B. wolffi* [1].
The genus *Bunium* (Apiaceae) comprises about 50 species of geophytes with tuberiform storage roots, distributed in the arid and subarid SW and central Asia, Europe, and North Africa [2,3].
One of the well-known *Bunium* species is *Bunium persicum* (Boiss.) B.Fedtsch. that its seeds and essential oil used in medicinal and nutrition industries. The main components of *B. persicum* seed oil from Iran are cumin aldehyde, γ-terpinen-7-al and α- terpinen-7-al [4,5]. Takayuki *et al*. reported antifungal activity of *B. persicum* seed oil [6]. Jamil *et al*. reported the antioxidative activity of *B. cylindricum* (Boiss. & Hohen.) Drude and *B. persicum* of Pakistani oils [7].
The oil of two cultivates of the seed of *B. cylinclricum* from Pakistan, was investigated with respect to percentage yield, physicochemical properties and composition. During floristic surveys at Cudi Mountain (Silopi/Cizre) from May to July 2017, some interesting *Bunium* specimens were collected. To determine those specimens, a wide range of literatures [5-7] were used. Finally, collected *Bunium* matterials were identified asHedge & Lamond which was firstly described from Cudi Mountain (Şilopi/Cizre). The white seed oil (1.4%) contained myristicin (67.2%) and limonene (13.7%), while the black seed oil (1.8%) contained elemicin (39.3 %), α-cadinene (13.4%), dillapiole (11.0 %) and β-selinene (10.9%) as major constituents [8].

*Corresponding author: Research Institute of Forests and Rangeland, Agricultural Research, Education and Extension Organization (AREEO) Tehran, Iran
Email Address: camcarjaimand@yahoo.com

Analyses of the essential oils of *B. elegans* (Fenzl) Freyn and *B. caroides* (Boiss.) Hausskn. ex Bornm., using GC, GC-MS, and 13C-NMR spectroscopy resulted in identification of their chemical constituents. The oils of both species contain mainly the sesquiterpene hydrocarbons germacrene-D and E-caryophyllene, which amounted to 24.1% and 38 % for *B. elegans* and 22.1 % and 26.6% for *B. caroides* respectively. The oil of *B. caroides* contained the monoterpenes α-pinene and Z-β-ocimene in 4.1 and 5.9% respectively, while traces of monoterpenes were detected for *B. elegans*. On the other hand, in *B. caroides* the phenylpropanoid derivatives asaricin (7.5%) and dillapiole (10.2 %) were among the major constituents [9].

In the seed oil of p-cymene and cuminaldehyde have been reported as the main constituents [10]. The fruit oil of *B. persicum* contained p-cymene (19.1%) and cuminaldehyde (40.7%) as the major components [10]. The major components found in the oil of *B. cylindricum* were myristicin (43.1%), β-phellandrene (20.0%), β-pinene (15.6%) and α-pinene (10.7%) [11].

The center of diversity of *Bunium* is in the Mediterranean region. It is spread in almost every part of Turkey, especially in the Southeastern Anatolia and Eastern Anatolia regions. *B. elegans* known as “Zireh” is a wild plant distributed in different parts of Iran, Anatolia and Iraq.

There are several studies on the chemotype development in various plants’ cultivars and differences in essential oils composition and biological activities between the cultivated and wild ones [12,13]. *B. persicum* ((Apiaceae) is a perennial herb, native to Iran, Pakistan and Afghanistan [14]. The small odorant fruits of *B. persicum* (“Zireh siah” or “Wild Caraway”) are traditionally used as antiseptic, carminative and condiment [15]. Several studies have previously determined essential oil composition of *B. persicum* and commonly reported γ-terpinene, cuminaldehyde and ρ-cymene as major compounds [16-17].

Moreover, the oil has demonstrated strong antibacterial activity against some gram positive and gram negative bacteria and also considerable insecticide effects [17,18].

Another research has investigated the essential oil composition of wild and cultivated *B. persicum* from India and shown some similarities and differences in oils, mainly the higher level of cuminaldehyde in cultivated fruits [19]. In a study exploring antioxidant components of the fruits, kaempferol, caffeic acid and p-coumaric acid were introduced as active ingredients from extract.[20]. Also, antimicrobial properties of these three compounds against some bacterial and fungal strains have been shown in some studies. [21-24].

Bunium sp. contained mostly monoterpenes and phenylpropanoids, such as *α*-pinene, *p*-cymene, limonene, *γ*-terpinene, cuminaldehyde, cuminyl alcohol, myristicin, and dillapiole. The essential oil of *B. cylindricum* from Pakistan, on the other hand, consisted mostly of myristicin, limonene, elemicin, dillapiole, and *β*-selinene. The essential oil of the *B. sp.* is used as a carminative and antiseptic [25].

In this research, Essential oil content and composition of two Iranian Bunium species named *B. kuhitangi* Nevski and and *B. microcarpum* (Boiss) Freyn & Bornm. were studied.

Material and Methods

Plant Material

The aerial parts of *B. kuhitangi* Nevski were collected from Golestan provience, Gorgan, Golestan park, Almeh, hight 1569 m, on 2 June 2020, and *B. microcarpum* (Boiss) Freyn & Bornm. Were collected from Golestan provience, Gorgan, Golestan park, Almeh, hight 1650 m, on 2 June 2020. The voucher specimens have been deposited in the national herbarium of Iran (TARI).

Isolation Procedure

Ariel parts of plant 50g were subjected to water-distillation for 3 h using a Clevenger-type apparatus. *B. kuhitangi*. oil yield were 1.03% and *B. microcarpum*. oil yield were 0.81%.

Gas Chromatography

GC analyses were performed using a gas chromatography, Ultera Fast Module –GC, made in Italia. Profile column machine brand Ph-5 capillary column, with 10 m, ID 0.1 mm, final temperature 0.4, oven: 60-285 °C/min., Rate: 40 °C/min., Hold time: 3 min., Run time: 8.63 min. Detector: FID, 280 °C, injector: 280 °C, carrier Gas: He, 0.5 mL/min. The carrier gas inlet pressure to the column: helium with a purity of 99/99% of the inlet pressure to the column equal to 5/1 kilogram per square centimeter is set.

Gas Chromatography-Mass Spectrometry

GC–MS analysis is performed on an Agilent 7890A/5975C GC-MS system equipped with a DB-5 fused silica column (30 m × 0.25 mm i.d., film thickness 0.25 µm). The oven temperature is programmed as follows: the initial temperature of 60 °C is immediately increased to 220 °C at a rate of 3 °C/min, subsequently the temperature is increased to 260 °C at 20 °C/min and held at this temperature for 3 min. The injector and transfer line temperature are 260 and 280 °C, respectively; carrier gas is helium with a linear velocity of 30.6 cm/s; split ratio 1:100, ionization energy 70 eV, scan time 1s, mass range 30–340 a.m.u.

Table 1 Chemical composition essential oils of *B. kuhitangi* Nevski and *B. microcarpum* (Boiss) Freyn & Bornm.

Compounds name	R.I.	*B. microcarpum*	*B. kuhitenoi*
Camphene	946	0.89	2.91
β- pinene	978	0.37	-
Hexyl acetate	1007	1.76	3.54
γ-terpinene	1055	0.35	-
Acetophenone	1058	0.43	-
Terpinen-4-ol	1177	-	2.49
p-menth-1-en-7-al	1272	-	0.95
2-undecanone	1292	-	3.26
293cis-piperitol acetate	1329	1.32	-
Thymol acetate	1348	-	0.65
Carvacrol acetate	1371	-	4.67
α- copaene	1377	-	8.38
(E)- caryophyllene	1415	0.29	-
Methyl undecanoate	1425	0.33	-
α- humulene	1452	-	0.92
9-epi-(E)- caryophyllene	1464	73.61	35.38
α-terpinyl isobutanoate	1470	1.69	0.93
δ- selinene	1494	-	7.35
n-pentadecane	1500	-	0.85
Sesquicineole	1517	0.32	-
(E)- iso- γ-bisabolene	1528	-	2.01
γ- cuprenene	1534	8.37	3.66
α-cadinene	1537	5.75	-
α- calacorene	1545	2.28	
Cis-cadinene ether	1551	1.54	0.85
Germacrene B	1559	-	1.14
Caryophyllene oxide	1581	-	5.52
α- muurolol	1644	0.64	-
(Z)- α- trans-bergamotol	1690	-	1.70
2-pentadecanone	1696	-	0.74
Isobicyclogermacrenal	1731	-	0.33
(E)- sesquilavandulyl acetat	1738	-	2.68
Cedryl acetate	1766	-	1.93
β-bisabolenal	1769	-	0.80
n-pentadecanol	1772	-	0.83
(Z)- α-santalol acetate	1778	-	1.56
n-nonadecane	1900	-	2.92
n-eicosane	2002	-	0.91

The identity of the oil components was established from their GC retention indices, relative to C7- C25 n-alkanes standards mixture, and by comparison of their mass spectra and retention indices with those reported in the literature [26-28], and by computer matching with the Wiley 5 and NIST mass spectra library, whenever possible, by co-injection with standards available in the laboratories.

Result

Main components of essential oil in table 1, from *B. kuhitangi* Nevski were 9-epi-(E)- caryophyllene (35.38%), α- copaene (8.38%) and δ- selinene (7.35%) and main components for *B. microcarpum* (Boiss) Freyn & Bornm. were 9-epi-(E)- caryophyllene (73.61%), γ- cuprenene (8.37%) and α-cadinene (5.75%). β-caryophyllene is a pale yellow oily liquid with an odor midway between odor of cloves and turpentine. To the best of our knowledge, this is the first report on the chemical constituents of *B. kuhitangi* from Iran.

Discussion

Main components from *B. kuhitangi* Nevski were 9-epi-(E)- caryophyllene (35.38%), α- copaene (8.38%) and δ- selinene (7.35%) and main components for *B. microcarpum* (Boiss) Freyn & Bornm. were 9-epi-(E)- caryophyllene (73.61%), γ- cuprenene (8.37%) and α- cadinene (5.75%). β-caryophyllene is a pale yellow oily liquid with an odor midway between odor of cloves and turpentine. Sefidkon, *et al*., 2014, reported on *B. microcarpum*, 23 components were characterized in the oil of the leaves and flowers of *B. microcarpum*. Elemicine (21.7%), germacrene D (12.7%), (Z)-β-ocimene (12.2%), limonene (11.8 %) and β-pinene (9.6 %) were the main constituents [29]. Finally, *B.* matterials were collected and identified as *B. microcarpum* which was firstly described from Cudi Mountain (Şilopi/Cizre). The white seed oil (1.4 %) contained myristicin (67.2%) and limonene (13.7 %), while the black seed oil (1.8 %) contained elemicin (39.3%), α-cadinene (13.4%), dillapiole (11.0%) and β-selinene (10.9 %) as major constituents [8]. Analyses of the essential oils of *B. elegans* (Fenzl) Freyn and *B. carioides* (Boiss.) Hausskn. main components in both species were sesquiterpene hydrocarbons germacrene-D and E-caryophyllene, which amounted to (24.1%) and (38%) for *B. elegans* and (22.1%) and (26.6%) for *B. caroides*, respectively. The oil of *B. caroides* contained the monoterpenes α-pinene (4.1%) and Z-β-ocimene (5.9%), respectively, while traces of monoterpenes were detected for *B. elegans*. On the other hand, in *B. caroides* the phenyl propanoid derivatives asaricin (7.5%) and dillapiole (10.2%) were among the major constituents [9]. In the seed oil of *B. hulbocastanum*, p-cymene and cuminaldehyde have been reported as the main constituents [10]. The fruit oil of *B.*

persicum contained p-cymene (19.1%) and cuminaldehyde (40.7%) as the major components [10]. The major components found in the oil of *B. cylindricum* were myristicin (43.1%), β-phellandrene (20.0%), β-pinene (15.6%) and α-pinene (10.7%) [11]. There are several studies on the chemotype development in various plants' cultivars and differences in essential oils composition and biological activities between the cultivated and wild ones [12,13]. Several studies have previously determined essential oil composition of *B. persicum* and commonly reported γ-terpinene, cuminaldehyde and ρ-cymene as major compounds [16-17]. *B.* sp. contained mostly monoterpenes and phenylpropanoids, such as *α*-pinene, *p*-cymene, limonene, *γ*-terpinene, cuminaldehyde, cuminyl alcohol, myristicin, and dillapiole.

In this research, Essential oil content and composition of two Iranian Bunium species named *B. kuhitangi* Nevski and and *B. microcarpum* (Boiss) Freyn & Bornm. were studied.

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