AkiNik

American Journal of Essential Oils and Natural Products

Available online at www.essencejournal.com

AJEONP

American Journal of Essential Oils and Natural Products

ISSN: 2321 9114
AJEONP 2015; 2 (3): 24-27

Received: 23-02-2015
Accepted: 14-04-2015

Farukh S. Sharopov
V. I. Nikitin Institute of Chemistry, Tajik Academy of Sciences Ainy st. 299/2, Dushanbe, 734063, Tajikistan.

Muhammadsho A. Kukaniev
V. I. Nikitin Institute of Chemistry, Tajik Academy of Sciences Ainy st. 299/2, Dushanbe, 734063, Tajikistan.

Hanjing Zhang
Department of Chemisry, University of Alabama in Huntsville Huntsville, AL 35899, USA.

William N. Setzer
Department of Chemisry, University of Alabama in Huntsville Huntsville, AL 35899, USA.

Correspondence:
William N. Setzer
Department of Chemisry, University of Alabama in Huntsville Huntsville, AL 35899, USA.
wsetzer@chemistry.uah.edu

Essential Oil Constituents of Zira (*Bunium persicum* [Boiss.] B. Fedtsch.) from Tajikistan

Farukh S. Sharopov, Muhammadsho A. Kukaniev, Hanjing Zhang, William N. Setzer

Abstract
The fruit essential oils from Tajik wild (TW) type and Indian commercial (IC) *Bunium persicum* were obtained by hydrodistillation and analyzed by gas chromatography – mass spectrometry. A total of 47 components were identified representing 99.8% of the TW type and 99.6% of the IC type, respectively. The compositions of TW and IC *B. persicum* oils were very similar and were composed largely of monoterpene hydrocarbons and oxygenated monoterpenoids. Cuminaldehyde was identified as a major component of the *B. persicum* oils, with a content of 36.0% TW and 29.9% IC. The other main components of this oils were found to be γ-terpinen-7-al (TW: 15.0% and IC: 17.2%) and α-terpinen-7-al (TW:13.1% and IC:8.1%), followed by γ-terpinene (TW:10.9% and IC:10.9%), β-pinene (TW: 9.1% and IC: 7.8%), and *p*-cymene (TW: 5.3% and IC: 12.5%).

Keywords: *Bunium persicum,* essential oil composition, cluster analysis, cuminaldehyde, γ-terpinen-7-al, α-terpinen-7-al, γ-terpinene.

1. Introduction
Bunium persicum (Zira, black cumin) is an important aromatic plant in the Apiaceae. *B. persicum* is a perennial herb with frilly leaves, hermaphroditic flowers, and a tuberous root at a soil depth of 10 cm. The plant can reach about 60 cm tall and 25 cm wide. *B. persicum* is distributed in the mountainous regions of Iran, Tajikistan, Afghanistan, Pakistan and the western part of Northern India (Kashmir, Punjab) and bears fruit that is an extremely popular seasoning for meat dishes in Central Asia. The seeds are also consumed widely as a condiment and are reported to work as a stimulant and carminatives, which is found to be useful in treating diarrhea and dyspepsia [1]. The plant offers several therapeutic effects on digestive and urinary tract disorders and is used for chronic diseases of the stomach (chronic gastritis), intestines (colitis), and liver (jaundice) as well as chronic cholangitis, swelling, and kidney stones in Tajikistan traditional medicine. In addition, tea made from *B. persicum* seeds is regarded as a popular means of increasing the appetite. Furthermore, the plant can enhance wound healing, and its continuous use prevents obesity.
B. persicum oil has been evaluated for antimicrobial activity [2], antifungal activity [3], antihistaminic activity [4], antibacterial activity [5], antioxidant activity [6, 7], pharmacological activity [8]. Previous studies on the chemical constitutions of *B. persicum* growing in Iran [5-7, 9-12], Tajikistan [1, 8, 13], Pakistan [14, 15], and India [16] have been reported. In this research we have analyzed the chemical compositions of oils of *B. persicum* seed from Tajik wild and Indian commercial types, and we have characterized the compositions with respect to previously reported samples using a cluster analysis.

2. Materials and Methods
2.1 Plant Material
The wild plant material of *B. persicum* (TW) was collected from the Dashtijum Mountain in the Shurobod region of Tajikistan (37.9967 N, 70.2101 E, 2400 m above sea level) in July 2010. Voucher specimens have been deposited (TJ2010-056) at the herbarium of the Chemistry Institute of the Tajikistan Academy of Sciences. The commercial sample (IC) was obtained from an Indian grocery store, Suraj Imports, Huntsville, Alabama. The oil samples were obtained from seed material by hydrodistillation.

2.2 Gas Chromatographic – Mass Spectral Analysis

A gas chromatographic-mass spectral analysis was performed on the essential oils of *B. persicum* using an Agilent 6890 GC with Agilent 5973 mass selective detector (EIMS, electron energy = 70 eV, scan range = 45-400 amu, and scan rate = 3.99 scans/s), and a fused silica capillary column (HP 5 ms, 30 m × 0.25 mm) coated with 5% phenyl-polymethylsiloxane (0.25 µm phase thickness). The carrier gas was helium with a flow rate of 1 mL/min, and the injection temperature was 200°C. The oven temperature was programmed to initially hold for 10 minutes at 40 °C, then ramp to 200 °C at 3°C/min and finally to 220°C at 2°C/min. The interface temperature was 280°C. A 1% w/v solution of each sample in CH_2Cl_2 was prepared, and 1 µL was injected using a splitless injection technique. Identification of the oil components was based on their retention indices determined by reference to a homologous series of *n*-alkanes, and by comparison of their mass spectral fragmentation patterns with those reported in the literature [17], and stored on the MS library [NIST database (G1036A revision D.01.00)/ChemStation data system (G1701CA, version C.00.01.080)]. The percentages of each component are reported as raw percentages based on total ion current without standardization. The chemical compositions of the *B. persicum* seed oils are summarized in Table 1.

Table 1: Gas chromatographic – mass spectroscopic analysis of *Bunium persicum* seed essential oils from Tajikistan and India.

Compound	RI[a]	RI[b]	Area (%)	
			TW[c]	IC[d]
Hexanal	801	801	tr	tr
Cumene	933	930	tr	tr
α-Thujene	935	930	0.4	0.3
α-Pinene	941	939	0.6	0.4
Camphene	954	954	tr	tr
β-Pinene	980	979	9.1	7.8
Myrcene	993	990	0.7	0.6
α-Phellandrene	1004	1002	0.1	0.2
δ-3-Carene	1010	1011	tr	tr
α-Terpinene	1016	1017	0.1	0.1
1-*p*-Menthene	1021	1026	tr	---
p-Cymene	1025	1024	5.3	12.5
β-Phellandrene	1029	1029	0.5	0.4
1,8-Cineole	1031	1031	0.3	0.2
Phenylacetaldehyde	1043	1042	tr	---
γ-Terpinene	1060	1059	10.9	10.9
cis-Sabinene hydrate	1067	1070	0.1	0.1
1-Octanol	1071	1072	tr	---
cis-Linalool oxide (furanoid)	1072	1088	---	tr
p-Mentha-2,4(8)-diene	1086	1089	tr	---
Terpinolene	1088	1092	0.1	0.1
6,7-Epoxymyrcene	1093	1098	tr	tr
trans-Sabinene hydrate	1097	1096	0.1	0.1
Linalool	1100	1110	0.1	0.1
p-1,3,8-Menthatriene	1111	1070	tr	---
cis-*p*-Menth-2-en-1-ol	1120	1121	0.1	0.1
trans-Pinocarveol	1137	1139	0.1	0.2
Pinocarvone	1161	1164	tr	tr
Terpinen-4-ol	1176	1177	0.2	0.3
Dill ether	1185	1186	tr	---
Cryptone	1185	1185	---	0.1
α-Terpineol	1190	1188	tr	0.1
Anthemol (= *p*-Mentha-1,3-dien-7-ol)	1194	---	5.8	9.5
Myrtenol	1195	1195	---	0.1
trans-Piperitol	1207	1208	tr	---
Cuminaldehyde	1241	1241	36.0	29.9
Carvenone	1255	1258	---	tr
p-Menth-1-en-7-al (= Phellandral)	1275	1275	0.6	0.1
p-Mentha-1,3-dien-7-al (= α-	1287	1285	13.1	8.1
p-Mentha-1,4-dien-7-al (= γ-	1296	1291	15.0	17.2
Carvacrol	1302	1299	---	tr
p-Mentha-1,4-dien-7-ol	1328	1327	0.6	0.1
Daucene	1381	1381	tr	tr
Cuminyl acetate	1423	1422	tr	---
(*E*)-β-Farnesene	1458	1456	tr	tr
10-*epi*-Acoradiene	1474	1475	0.1	0.1
Carotol	1596	1594	tr	Tr

[a] Retention Indices on HP-5ms fused silica capillary column
[b] Ref [17]
[c] Tajikistan wild *Bunium persicum*
[d] Indian commercial *Bunium persicum*

2.3 Hierarchical Cluster Analysis

A selection of 31 *B. persicum* essential oil compositions from the published literature [1, 5-7, 9, 11, 16, 18-26] were treated as operational taxonomic units (OTUs). The percentage composition of 13 monoterpenoid essential oil components (α-pinene, sabinene, β-pinene, myrcene, *p*-cymene, limonene, 1,8-cineole, γ-terpinene, terpinolene, anthemol, cuminaldehyde, α-terpinen-7-al, and γ-terpinen-7-al) was used to determine the chemical relationship between the different *B. persicum* essential oil samples by agglomerative hierarchical cluster (AHC) analysis using the XLSTAT software, version 2014.4.09. Pearson correlation was selected as a measure of similarity, and the unweighted pair-group method with arithmetic average (UPGMA) was used for cluster definition. The *B. persicum* dendrogram is shown in Figure 1.

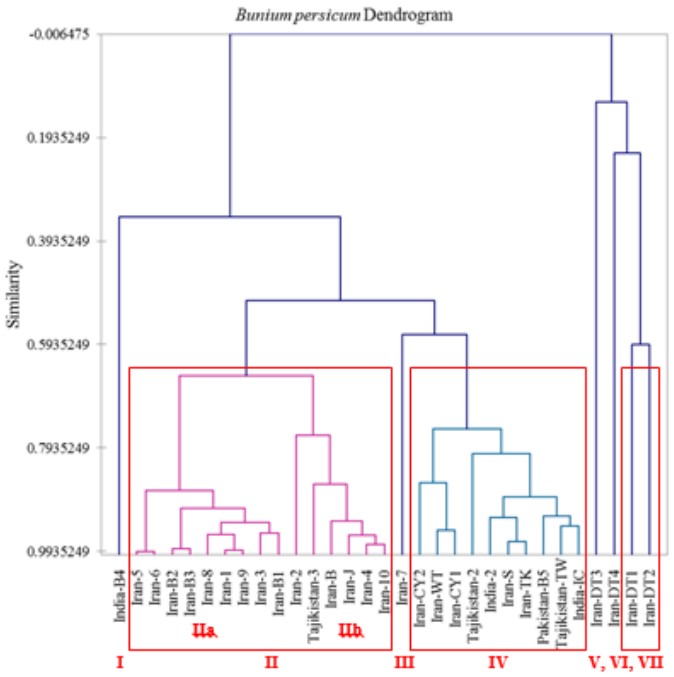

Fig 1: Dendrogram obtained from the agglomerative hierarchical cluster analysis of 31 *B. persicum* seed essential oil samples: Tajikistan-TW, India-IC (this work); Tajikistan-3 [1]; Iran-3 [5]; Iran-9 [6]; Iran-8 [7]; Iran-WT, Iran-CY1, Iran-CY2 [9]; Iran-1 [11]; India-2 [16]; Iran-2 [18]; Iran-4, Iran-10 [19]; Iran-5 [20]; Iran-6 [21]; Iran-7 [22]; Iran-DT1, Iran-DT-2, Iran-DT3, Iran-DT4 [23]; Iran-J, Iran-B, Iran-S, Iran-TK [24]; Iran-B1, Iran-B2, Iran-B3, India-B4, Pakistan-B5 [25]; Tajikistan-2 [26].

3. Results and Discussion

The composition of *B. persicum* seed oils of the Tajik wild (TW) and Indian commercial (IC) types were analyzed by GC-MS. In total, 42 TW and 39 IC compounds were identified, representing 99.8% of the TW type and 99.6 % of the IC type, respectively. The GC-MS characterization of the *B. persicum* oils (Table 1) reveals the oils to be dominated by monoterpene hydrocarbons and oxygenated monoterpenoids. Cuminaldehyde was identified as a major component of the *B. persicum* oils, with a content of 36.0% TW and 29.9% IC. The other main components of this oil were found to be γ-terpinen-7-al (TW: 15.0% and IC: 17.2%) and α-terpinen-7-al (TW: 13.1% and IC: 8.1%), followed by γ-terpinene (TW: 10.9% and IC: 10.9%), β-pinene (TW: 9.1% and IC: 7.8%), and *p*-cymene (TW: 5.3% and IC: 12.5%). The components of the Tajik wild (TW) and Indian commercial (IC) types of *B. persicum* oils are qualitatively similar, with the TW type showing the same amount of γ-terpinene; a unmistakably higher concentration of cuminaldehyde and α-terpinen-7-al; and a lower concentration of *p*-cymene compared to that of the IC type.

A number of studies on the essential oil content and components of *B. persicum* have been reported in the literature. Baser and co-workers [1] have analyzed *B. persicum* oil originating from Tajikistan, detecting 22 compounds, including γ-terpinen-7-al (29.0%), γ-terpinene (25.7%), β-pinene (15.6%), and cuminaldehyde (11.7%); in qualitative agreement with the results of the current study. Baser investigated two chemotypes of BPEO from Tajikistan. In his work, ripe fruits of *Bunium persicum* collected in Tajikistan yielded 7.3% oil, which contained cuminaldehyde (40.7%) and *p*-cymene (19.2%) as the main components. Baser detected a similar amount of cuminaldehyde but a significant higher amount of *p*-cymene compared to this study. Another chemotype of BPEO from Kulob (Tajikistan) yielded 3.3% oil in which γ-terpinen-7-al (29.0%), γ-terpinene (27.7%), β-pinene (15.6%), cuminaldehyde (11.7%), and *p*-mentha-1,3-dien-7-al (5.1%) were the main components [1]. This type of BPEO contain significantly higher amount of γ-terpinen-7-al, γ-terpinene, and β-pinene than that measured in this study (15.0% for γ-terpinen-7-al, 10.9% for γ-terpinene, and 9.1% for β-pinene). However, our investigation shows a much higher amount of cuminaldehyde (36.0%).

In order to put the chemical compositions of *B. persicum* seed essential oils into perspective, a hierarchical cluster analysis was carried out (Figure 1). The cluster analysis reveals at least seven different chemotypes: **I**, rich in α-terpinen-7-al; **II**, dominated by γ-terpinene with limonene, *p*-cymene, and cuminaldehyde; **III**, dominated by *p*-cymene; **IV**, rich in cuminaldehyde as well as γ-terpinene and γ-terpinen-7-al; **V**, rich in α-pinene; **VI**, rich in γ-terpinen-7-al; and **VII**, rich in β-pinene and cuminaldehyde. Cluster **II** can be further subdivided into a sub-cluster with diminished γ-terpinen-7-al (**IIa**) and one with abundant γ-terpinen-7-al (**IIb**). Cultivated samples appear in cluster **IV** (e.g., CY1 and CY2 from Iran and IC from India).

4. Conclusions

Zira, *Bunium persicum*, is an important spice and herbal medicine. There are at least seven distinct chemotypes of *B. persicum* based on the essential oil compositions, and the essential oil from *B. persicum* from Tajikistan, as revealed in this study, is comparable in composition to cultivated samples from Iran or from India, rich in *p*-cuminaldehyde, γ-terpinen, and γ-terpinen-7-al.

5. Acknowledgments

FSS is grateful to the Fulbright Program for a generous research/travel grant. WNS is grateful to an anonymous private donor for the gift of the GC-MS instrumentation.

6. References

1. Baser KHC, Özek T, Abduganiev BE, Abdullaev UA, Aripov KN. Composition of the essential oil of *Bunium persicum* (Boiss.) B. Fedtsch. from Tajikistan. Journal of Essential Oil Research 1997; 9:597-598.
2. Syed M, Hanif M. Antimicrobial activity of the essential oil of the Umbelliferae family. Part 1. *Cuminum cyminum*, *Coriandrum sativum*, *Foeniculum vulgare* and *Bunium persicum* oils. Pakistan Journal of Scientific and Industrial Research 1985; 55:116-120.
3. Sardari S, Armin G, Micetich RG, Daneshtalab M. Phytopharmaceuticals, Part 1. Antifungal activity of selected Iranian and Canadian plants. Pharmaceutical Biology 1998; 36(3):180-188.
4. Boskabady MH, Moghadas A. Inhibitory effect of *Bunium persicum* on histamine (H1) receptors of guinea pig tracheal chains. Phytomedicine 2004; 11:411-415.
5. Oroojalian F, Kermanshahi RK, Azizi M, Bassami MR. Phytochemical composition of the essential oils from three Apiaceae species and their antibacterial effects on food-borne bacterial borne pathogens. Food Chemistry 2010; 120(3):765-770.
6. Sharififar F, Yassa N, Mozaffarian V. Bioactivity of major components from the seeds of *Bunium persicum* (Boiss.) Fedtch. Pakistan Journal of Pharmaceutical Sciences 2010; 23(3):300-304.
7. Shahsavari N, Barzegar M, Sahari MA, Naghdibadi H. Antioxidant activity and chemical characterization of essential oil of *Bunium persicum*. Plant Foods for Human Nutrition 2008; 63:183-188.
8. Khaidarov KK, Sadykov YD, Lebedeva LD, Ismailova MB. Composition and pharmacological activity of essential oil derived from *Bunium persicum* (Boiss.) B. Fedsch fruits. Khimiko-Farmatsevticheskii Zhurnal 1991; 25(9):73-75.
9. Azizi M, Davareenejad G, Bos R, Woerdenbag HJ, Kayser O. Essential oil content and constituents of black zira (*Bunium persicum* [Boiss.] B. Fedtsch.) from Iran during field cultivation (domestication). Journal of Essential Oil Research 2009; 21:78-82.
10. Foroumadi A, Asadipour A, Arabpour F, Amanzadeh Y. Composition of the essential oil of *Bunium persicum* (Boiss.) B. Fedtsch. from Iran. Journal of Essential Oil Research 2002; 14:161-162.
11. Pourmortazavi SM, Ghandiri M, Hajimirsadeghi SS. Supercritical fluid extraction of volatile components from *Bunium persicum* Boiss. (Black cumin) and *Mespilus germanica* L. (Medlar) seeds. Journal of Food Composition and Analysis 2005; 18:439-446.
12. Moghtader M, Iraj Mansori A, Salari H, Farahmand A. Chemical composition and antimicrobial activity of the

essential oil of *Bunium persicum* Boiss. Seed. Iranian Journal of Medicinal and Aromatic Plants 2009; 25(1):20-28.
13. Sadykov YD, Kurbanov M, Khavizov K, Regovatov YM. Composition of the essential oil from fruits of *Bunium persicum* (Boiss.) B. Fedtsh. Reports of Tajikistan Academy of Sciences 1978; 21(5):33-36.
14. Karim A, Pervez M, Bhatty MK. Studies on the essential oils of the Pakistani species of the family Umbelliferae, part 10. *Bunium persicum* Boiss. (Sah Zira) seed oil. Pakistan Journal of Scientific and Industrial Research 1977; 20(2):106-108.
15. Jamil R, Ahmad M, Saeed MA, Younas M. Antioxidative activity of essential oils of some species of Umbelliferae family of Pakistan: Part I. Journal of the Chemical Society of Pakistan 1991; 13(1):56-59.
16. Thappa RK, Ghosh S, Agarwal SG, Raina AK, Jamwal PS. Comparative studies on the major volatiles of kalazira (*Bunium persicum* seed) of wild and cultivated sources. Food Chemistry 1991; 41:129-134.
17. Adams RP. Identification of Essential Oil Components by Gas Chromatography / Mass Spectrometry, 4th Ed., Allured Publishing, Carol Stream, Illinois, 2007.
18. Salehi P, Mohammadi F, Asghari B. Seed essential oil analysis of *Bunium persicum* by hydrodistillation-headspace solvent microextraction. Chemistry of Natural Compounds, 2008; 44(1):111-113.
19. Chizzola R, Saeidnejad AH, Azizi M, Oroojalian F, Mardani H. *Bunium persicum*: variability in essential oil and antioxidants activity of fruits from different Iranian wild populations. Genetic Resources and Crop Evolution 2014; 61:1621-1631.
20. Mazidi S, Rezaei K, Golmakani MT, Sharifan A, Rezazadeh Sh. Antioxidant activity of essential oil from black zira (*Bunium persicum* Boiss.) obtained by microwave-assisted hydrodistillation. Journal of Agriculture Science and Technology 2012; 14:1013-1022.
21. Behtoei H, Amini J, Javadi T, Sadeghi A. Composition and *in vitro* antifungal activity of *Bunium persicum*, *Carum copticum* and *Cinnamomum zeylanicum* essential oils. Journal of Medicinal Plants Research 2012; 6(37):5069-5076.
22. Nickavar B, Adeli A, Nickavar A. Analyses of the essential oil from *Bunium persicum* fruit and its antioxidant constituents. Journal of Oleo Science 2014; 63(7):741-746.
23. Saeidnejad AH, Kafi M, Khazaei HR, Pessarakli M. Effects of drought stress on quantitative and qualitative yield and antioxidative activity of *Bunium persicum*. Turkish Journal of Botany 2013; 37:930-939.
24. Omidbaigi R, Arvin MJ. Effect of growing locations on the essential oil content and chemical compositions of *Bunium persicum* Boiss wild growing in Iran. Journal of Essential Oil-Bearing Plants 2009; 12(1):34-40.
25. Jahansooz F, Sefidkon F, Najafi A, Ebrahimzadeh H, Najafi MS. Comparison of essential oils of *Bunium persicum* (Boiss.) populations grown in Iran, Pakistan, and India. Journal of Essential Oil-Bearing Plants 2012; 15(5):761-765.
26. Abduganiev BE, Rashkes YaV, Plugar VN. GC-MS analysis of the essential oil of the fruit of *Bunium persicum*. Chemistry of Natural Compounds 1994; 30(2):269-270.