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CHEMICAL COMPOSITION OF THE ESSENTIAL OILS OF *Bunium elegans* AND *Bunium caroides*

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Analyses of the essential oils of Bunium elegans *(Fenzl) Freyn and* B. caroides *(Boiss.) Hausskn. ex Bornm., using GC, GC/MS, and* ^{13}*C-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.*

Key words: Umbelliferae, Apiaceae, *Bunium elegans*, *Bunium caroides*, essential oil, ^{13}C-NMR, GC/MS.

The genus *Bunium* L. belongs to the family Apiaceae and consists of 14 species in Iranian flora, two of which are endemic [1]. This genus is close to *Carum. Bunium* and *Carum* are two of the most important aromatic and medicinal plants, whose seeds and essential oils have been used in food and medicine all over the world for so long [2]. *Bunium elegans* (Fenzl) Freyn is a wild plant distributed in different parts of Iran, Anatolia and Iraq. *B. caroides* (Boiss.) Hausskn. ex Bornm. is grown wild in Syria and Transcaucasia as well [1].

To the best of our knowledge there are no reports in the literature on the chemical constituents of the above mentioned plants. *Bunium persicum* is a medicinal plant of Iran called "*Zireh*" [2]. The chemical constituents [3–10] and antioxidant and antiinflammatory properties [9] of the essential oil of *B. persicum* were studied by several authors. The chemical constituents of the oil of *B. persicum* collected from Iran contained mostly monoterpenes and phenylpropanoids, such as α-pinene, *p*-cymene, limonene, γ-terpinene, cuminaldehyde, cuminyl alcohol, myristicin, and dillapiole [10]. The essential oil of *B. cylindricum* from Pakistan, on the other hand, consisted mostly of myristicin, limonene, elemicin, *l*-cadinene, dillapiole, and β-selinene [3]. The oil of the medicinal plant "*Zireh*" is used in folk medicine as a carminative and antiseptic [10]. In order to investigate the chemical constituents and biological activities of the essential oils of the wild plants of Iran for their potential in medicinal use, we investigate the chemical constituents of the two *Bunium* species for the first time.

Hydrodistillation of aerial parts of *B. caroides* and *B. elegans* resulted in extraction of two oils in 0.14% and 0.13% yields, respectively. The oils after preparation were subjected to GC and GC/MS analysis. Identification of the chemical constituents was performed by comparison of their GC retention indices and mass spectra obtained from GC/MS. The oil of *B. elegans* was subjected to ^{13}C-NMR spectroscopy. The major constituents were further identified by ^{13}C-NMR spectral data. Identification of the constituents was confirmed by comparison of the GC [11], mass spectrometry [12–15], and ^{13}C-NMR data [16] with those reported in the literature.

Nineteen and 30 constituents were identified in the oils of *B. elegans* and *B. caroides*, respectively. The oils of both species contained mainly sesquiterpene. Germacrene-D and E-caryophyllene 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 monoterpenes, 14.4% of the oil, while traces of monoterpenes, 1.6% of the total oil, were detected for *B. elegans*.

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TABLE 1. Constituents of the Essential Oils of *B. caroides* and *B. elegans*

Compound	RRI	FID % *B.elegans*	RRI	FID % *B.caroides*	Compound	RRI	FID % *B.elegans*	RRI	FID % *B.caroides*
α-Pinene	-	-	**939**	**4.1**	4,8-β-Epoxycaryophyllene	-	-	1436	Tr.
Sabinene	-	-	974	0.2	β-Copaene	1440	Tr.	-	-
n-Octanal	985	0.3	-	-	Z-β-Farnesene	-	-	1450	1.0
β-Pinene	-	-	980	0.2	α-Humulene	1464	2.4	1464	1.6
Myrcene*	-	-	986	1.4	γ-Gurjunene	1484	Tr.	-	-
α-Phellandrene	-	-	1005	0.2	**Germacrene D***	**1494**	**38.0**	**1491**	**26.6**
p-Cymene	-	-	1019	Tr.	**Asaricin*+γ-Amorphene**	-	-	**1499**	**7.5**
Z-β-Ocimene*	-	-	**1029**	**5.9**	**Bicyclogermacrene**	**1506**	**8.3**	**1504**	**2.5**
E-β-Ocimene	-	-	1041	1.1	**Germacrene A**	-	-	**1522**	**2.5**
γ-Terpinene	-	-	1055	0.2	δ-Amorphene	1524	0.8	1524	Tr.
Terpinolene	-	-	1086	0.9	Nerolidol	-	-	1566	0.4
Linalool	1088	0.2	1088	Tr.	Silphiperfol-5-en-3-ol A	1571	0.7	-	-
Borneol	1159	0.2	1160	0.2	**Spathulenol**	**1580**	**4.3**	1578	0.4
Bornyl acetate	1277	1.2	-	-	**Caryophyllene oxide**	**1588**	**5.9**	1586	1.6
δ-Elemene	1343	0.3	1343	Tr.	Thujopsan-2-α-ol	1594	0.8	1594	Tr.
α-Copaene	1387	1.3	1386	0.5	**Dillapiole***	-	-	**1603**	**10.2**
β-Elemene	-	-	1397	0.6	14-Hydroxy-9-*epi*-(E)-caryophyllene	1682	1.2	-	-
β-Cubebene	1397	1.4	-	-	Cyclopentadecanolide	-	-	1839	0.4
E-Caryophyllene*	**1435**	**24.1**	**1433**	**22.1**	Total		91.4		92.3

*Identifications confirmed by ^{13}C-NMR.

In addition to monoterpenes in the oil of *B. caroides* the phenylpropanoid derivatives asaricin (7.5%) and dillapiole (10.2%) were detected in higher amounts. In the ^{1}H- and ^{13}C-NMR spectra of the oil of *B. caroides* the signals of asaricin and dillapiole were more intense than the signals of other constituents.

EXPERIMENTAL

B. elegans was collected on Zanjan-Bijar road, about 40 km from Zanjan at altitude 1900 m in June 2003. *B. caroides* was collected in Takab-Shahindej at altitude 2300 m in May 2003. The plant materials were identified by one of us (A. S.) in the department of biology of MPRI. A voucher specimen has been deposited for each of the plants in the herbarium of the institute (herbarium nos. 2003–70 and 2003–71 for *B. elegans* and *B. caroides*, respectively). The shade-dried aerial parts of the plants (*B. elegans*, 70 g, *B. caroides*, 75 g) were extracted by hydrodistillation for 3 h, yielding yellow color oils in 104 and 93 mg amounts, respectively. The oils were dried over anhydrous sodium sulfate before submission to GC, GC/MS, and ^{13}C-NMR analyses.

Gas Chromatography Analysis. Gas Chromatography was performed on a Varian CP-3800 chromatograph, with a FID and a CP Sil 5CB column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The oven temperature was programmed from 60°C to 250°C at 5°C/min and kept 10 min at this temperature. The carrier gas was N_2 with a flow rate of 1.1 mL/min. Injector and detector temperature were set at 280°C. The injection volume was 3 μL for the oils and *n*-alkanes for calculation of the retention indices.

Gas Chromatography-Mass Spectroscopy Analyses. The GC-MS was carried out on a Thermo Finnigan-trace GC coupled to a trace mass spectrometer operating in EI mode at 70 ev. The column was an RTX1 with the same dimensions as those for the GC with 60 m length. Helium was used as the carrier gas and the oven temperature was the same as for the analytical GC.

The ^{13}C-NMR (Broad Band and DEPT) experiments were measured in $CDCl_3$ on a Bruker 300 MHz NMR spectrometer.

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