Pakistan J. Sci. Ind. Res., Vol. 22, No. 6, December 1979

STUDIES ON THE ESSENTIAL OILS OF THE PAKISTANI SPECIES OF THE FAMILY UMBELLIFERAE

Part XXXVIII. *Bunium cylindricum*, (Boiss & Hoh), Drude (Zira khar) Seed Oil

Amna Karim, Muhammad Ashraf and Muhammad Khurshid Bhatty

PCSIR Laboratories, Lahore 16

(Received July 3, 1979)

The essential oil of two varieties of the seed of *Bunium cylindricum*, with 1.4 and 1.8% yield, has been investigated with respect to its percentage yield, physicochemical properties and chemical composition. T' e *Safed (white) zira khar* is composed of α-pinene (2.3%), camphene (1.0%), myrcene (0.7%), ⇐3-carene (0.7%), α-phellandrene (0.5%), limonene (13.7%), γ-terpinene (3.5%) *p*-cymene (1.4%), unidentified monoterpene (0.4%), myristicin (67.2%), dillapiole (traces), cuminaldehyde (2.1%), unknown ketone (1.1%), elemol (4.0%) and juniper camphor (1.1%) while the *siah (black zira khar)* contains α-pinene (0.3%), camphene (0.3%), Δ^3-carene (0.2%), limonene (0.7%), γ-terpinene (0.6%), unknown monoterpenes (0.3%), β-elemene (0.6%), β-caryophyllene (4.5%), humulene (2.7%), β-selinene (10.9%), *l*-cadinene (13.4%), bornyl acetate (1.0%), myristicin (4.1%), dillapiole (11.0%), elemicin (39.3%), an unknown ketone (0 9%), elemol (3.0%) and juniper camphor (6.2%). The seed of these species are chiefly used as an adulterant of *Bunium persicum*.

INTRODUCTION

Bunium, with 30—40 species, in is taxonomically a difficult genus. The species are found in the Mediterranean region, North Africa, South and Middle Europe, Iran, Afghanistan and Pakistan. Only three species namely *Bunium chaerophylloides, Bunium cylindricum* and *Bunium persicum* have been found to grow in Pakistan. The plants are perennial herbs.

Bunium cylindricum is a wild growing plant of the dry region around Quetta. Two types of the seed of the species are met with; one is black and other lighter in colour but comparatively larger in size. Locally, the seeds are called *Siah zira khar* and *Safed zira khar* respectively. Both are used as adulterants of *Bunium persicum*.

These sutdies have been undertaken because even though large quantities of the seeds of these species are brought to local markets annually, yet little is known about the quality and chemical composition of the essential oils obtained from the species. This communication, therefore, provides a detailed physicochemical evaluation of the essential oils distilled from the seeds of the two varieties of *Bunium cylindricum*.

MATERIALS AND METHODS

The seeds of the two species of *Bunium cylindricum* were collected from the Quetta market. The oil was re covered by dry steam-distillation according to the standard procedure [1]. In both cases a part of the oil was heavier than water, so the whole distillate was extracted with diethyl ether. The total ether extract was dried (sodium sulphate) and the oil freed from the solvent. The general methods used for the analysis of the oils are described in our earlier publications [1,2].

The essential oils recovered from both varieites of the seeds were subjected to fractionation by column chromatography using silica gel as an adsorbent. The hydrocarbons were further resolved into monoterpenes and sesquiterpenes by GLC using a column (3 mm X 3 m) packed with 20% carbowax on Chromosorb G, nitrogen as the carrier gas and flame ionisation detector. The individual terpenes were identified against their standard samples. The oxygenated components of the oil were recovered from the column with progressively increasing proportions (2—50%) diethyl ether in n-hexane. The fractions containing more than one components were rechromatographed to obtain single compounds. The various oxygenated components of the two oils were identified by TLC, GLC and IR and also by preparing their known derivatives.

RESULTS

The physicochemical properties and chemical composition of the essential oils obtained from the seeds of the

Table 1. Percentage yield and physicochemical values of the essential oils of *Bunium cylindricum* seeds of two varieties.

Values	Oil recovered from	
	Siah zira khar	Safed zira khar
Distillation period (hr)	30	30
Yield of oil (%)	1.8	1.4
Specific gravity	1.0488^{35}	0.9476^{28}
Refractive index	1.5100^{35}	1.5105^{28}
Optical rotation	$+ 4^{o} 16^{35}$	$+ 11^{o} 28$
Acid value	4.70	2.15
Ester value	18.00	9.20
Easter value after acetylation	51.50	51.30

The superscripts indicate the temperature at which these parameters were determined.

two species of *Bunium cylindricum* are recorded in Tables 1 and 2.

DISCUSSION

The two varieties of *Bunium cylindricum* give slightly different yields of the essential oil. Both oils have somewhat similar physical values, i.e. specific gravity, refractive index and optical rotation. The acid and ester values for the 'siah zira khar' are, however, much higher than those for the 'safed zira khar', indicating the presence of more free acid and ester in the oil of the former. This observation was further supported by IR of the 'siah zira' oil which showed strong absorption at 5.7 and 8.1 nm. The IR of the 'safed zira khar' showed a peak at 5.9 nm, indicating the presence of carboxylic compounds.

The two oils do not only differ in hydrocarbon fraction but also have different oxygenated compounds. The hydrocarbons of the 'siah zira khar' are composed of monoterpenes and sesquiterpenes in which the sesquiterpenes constitute the major portion. The hydrocarbon of the 'safed zira khar' are totally free from sesquiterpenes and are mainly composed of monoterpenes.

Geranyl acetate is the only ester which has been identified in the essential oil of 'siah zira khar' but its presence in the 'safed zira khar' could not be ascertained. The ester was identified by TLC, GLC and IR comparison with its authentic sample. It was also hydrolyzed with 0.1*N* alcoholic KOH and the parent alcohol, geraniol, was identified by IR comparison with its standard spectrum.

Myristicin is one of the major components (67.2% of the total oil) of the 'safed zira khar' oil but its amount is only 4.1% in the 'safed zira khar' oil. Myristicin was identified by IR comparison with its standard spectrum and also by converting into its tetrabromide, m.p. 128°. Elemicin is found to be the major component of the essential oil of 'siah zira khar' and is totally absent in the 'safed zira khar' oil. Elemicin was identified by IR comparison with its standard spectrum. Dillapiole is the common constituent of the two oils. It was identified by IR against its standard sample extracted from the essential oil of *Anethum raveolens*[3] (dill).

The essential oil of the 'safed zira khar' also contains cuminaldehyde which is again absent in the 'siah zira khar' oil. However, both oils contain 3–4% unidentified ketones.

Table 2. Percentage composition of the essential oils of *Bunium cylindricum* seeds of two varieties.

Eluent	Component	Oil recovered from	
		Siah zira khar (%)	Safed zira khar (%)
n-Hexane	Hydrocarbons*	34.5	24.2
	Unidentified monoterpene	0.1	0.2
	-do-	0.2	0.2
	α-Pinene	0.3	2.3
	Camphene	0.3	1.0
	Myrcene	–	0.7
	Δ^3-Carene	0.2	0.7
	α-Phellandrene	–	0.5
	Limonene	0.7	13.7
	γ-Terpinene	0.6	–
	p-Cymene	–	1.4
	β-Elemene	0.6	–
	β-Caryophyllene	4.5	–
	Humulene	2.7	–
	β-Selinene	11.0	–
	l-Cadinene	13.3	–
1% Diethyl ether in n-hexane	Bornyl acetate	1.0	–
2% Diethyl ether in n-hexane	Myristicin	4.1	67.2
2% Diethyl ether in n-hexane	Dillapiole	11.0	Traces
3% Diethyl ether in n-hexane	Elemicin	39.3	–
4% Diethyl ether in n-hexane	Unknown ketones	0.9	1.1
50% Diethyl ether in n-hexane	Elemol	3.0	4.0
50% Diethyl ether in n-hexane	Juniper camphor	6.2	1.1

*Resolved and estimated by GLC.

The essential oils of the 'siah zira khar' contains a sesquiterpene alcohol, elemol, which is not present in the essential oil obtained from the 'safed zira khar'. The alcohol was identified by IR comparison with its standard spectrum. The sesquiterpene alcoholic fraction of the oil was eluted from the column with 50% diethyl ether in n-hexane. This fraction also contained another solid hydroxy compound. It was crystallized from diethyl ehter – hexane (1:1) and it gave m.p. 164–166° (lit [4]. m.p. 166°). The compound was identified as juniper camphor by IR comparison with an authentic sample. Juniper camphor is again a common constituent of the two essential oils of *Bunium cylindricum.*

Acknowledgements. We are grateful to the United States Department of Agriculture for financing this research under a PL-480 Scheme and to Mr. Abdul Waheed Sabir, our Botanist, for the identification and procurement of authentic samples for these studies.

REFERENCES

1. M. Ashraf and M.K. Bhatty, Pakistan J. Sci. Ind. Res., **18**, 232 (1975).
2. M. Ashraf and M.K. Bhatty, Pakistan J. Sci. Ind. Res., **18**, 236 (1975).
3. M. Ashraf, J. Aziz and M.K. Bhatty, Pakistan J. Sci. Ind. Res., **20**, 52 (1977).
4. K.R. Verma, T.C. Jain and S.C. Bhattacharyya, Tetrahedron, **18**, 979 (1962).