

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

Part X. *Bunium Persicum* Boiss (Siah Zira) Seed Oil

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Abstract. The essential oil of *Bunium persicum* Boiss (Siah zira), which is a common plant of the cold arid regions of Pakistan, has been studied for the first time with respect to its physicochemical constants and chemical composition. The seeds of *B. persicum* from Gilgit, Swat, Zarghoon and Ziarat contain 7.1, 5.3, 7.1 and 7.2% of essential oil respectively. While the Gilgit, Swat and Zarghoon oils in this order contain α -pinene (0.0, 0.1 and 0.2%), β -pinene (1.0, 0 and 0%), Δ^3 -carene (0, 0.9 and 0.3%), limonene (0.3, 24.2 and 29.8%), γ -terpinen (19.8, 28.9 and 25.0%), *p*-cymene (32.8, 14.4 and 12.4%), cuminaldehyde (22.5, 17.8 and 14.8%), 1-4, *p*-menthadiene-7-al (1.2, 3.5 and 4.2%), 1,3 *p*-menthadiene-7-al (4.8, 5.6 and 7.2%), linalool (0, 2.0 and 0.4%) and eumynyl alcohol (0, 1.0 and 5.7%) the Ziarat oil contains α -pinene (2.0%), β -pinene (2.9%), Δ^3 -carene (1.8%), limonene (3.6%), β -phellanderene (0.6%), γ -terpinene (24.0%), *p*-cymene (41.1%), myristicin (2.0%), dillapiole (4.0%), linalool (16.0%) and carvacrol (1.0%). The seeds of *Bunium persicum* are comparable with cumin seeds as a species and yield a higher percentage of the essential oil.

Bunium persicum Boiss is a common plant of the cold and dry regions of Pakistan namely Gilgit, Baltistan, Chitral, Swat, Hazara and Baluchistan.

The seeds of *B. persicum*, in relation to cumin, are dark brown in colour and have a peculiar, heavy and warm flavour similar to but stronger than cumin seeds. The seeds have widely replaced the cumin seeds in flavouring curries in Pakistan, due to their strong flavour. The essential oil of *B. persicum* has nearly the same properties as those of cumin seeds. The plants from Ziarat, Baluchistan grow in the "Juniper zone" and the seeds have a different smell, but morphologically, these plants are similar to those found in the parts of the country.¹

In spite of its commercial importance, *B. persicum* has so far received little attention as an industrial crop of Pakistan and no attention has been paid to the cultivation of this species on a commercial scale. Some 200-300 tons of the seeds of the wild growing *B. persicum* are, nevertheless, annually collected in August and September to meet the local requirements. This amount can, however, be increased if these areas where it grows wild are protected from grazing. The present studies have been carried out with a view to determining the quality and chemical composition of the essential oils of *B. persicum* of Pakistan, indicating its qualitative and quantitative status in relation to other similar oils. These are the first studies of this kind not only in Pakistan and India, but also in the world.

Experimental

Materials and Methods. Fresh and mature seeds of *B. persicum* were directly collected from Gilgit, Swat, Zarghoon and Ziarat. The essential oil from the crushed materials was obtained according to the standard method.² The general methods employed

for these studies have been communicated in our earlier papers.^{2,3}

The essential oils from the seeds of the four localities were fractionated into hydrocarbon fractions and oxygenated components by silica gel column chromatography. The hydrocarbon fractions were further resolved into individual components by GLC using 3 mm x 3 m copper column packed with 20% polyethylene glycol succinate (BDH) on celite (60-80 mesh), nitrogen as the carrier gas and flame ionisation detector. The column temperature was maintained at 120°. The oxygenated components of the oils were identified by IR comparison and conversion into known compounds.

Results

The physicochemical properties and the chemical composition of the oils are recorded in Tables 1-3, GLC resolution of the hydrocarbon fraction of the essential oil of Ziarat is given in Fig. 1.

Discussion

The essential oil from the seeds of Gilgit, Swat and Zarghoon are pale yellow in colour with warm heavy smell similar to that of the cumin oil while Ziarat seed oil is almost colourless with very pleasant smell similar to coriander.

All the oils display somewhat similar physical properties. The acid value of the Gilgit oil is relatively high indicating the presence of considerable amount of free acids. The observation was further confirmed by chemically isolating cuminic acid from the Gilgit oil. The ester value after acetylation of the Ziarat oil is high showing the presence of higher amounts of hydroxy compounds.

The effect of ecological conditions on the com-

TABLE 1. PERCENTAGE YIELD AND PHYSICO-CHEMICAL PROPERTIES OF *Bunium persicum* ESSENTIAL OILS FROM GILGIT, SWAT, ZARGHOON AND ZIARAT REGION.

| Constant | Gilgit oil | Swat oil | Zarghoon oil | Ziarat oil |
|-------------------------------|----------------------|-----------------------|-----------------------|----------------------|
| Yield (max) | 7.1% | 5.3% | 7.1% | 7.2% |
| Distillation time | 7-10 hr | 7-10 hr | 8-10 hr | 8-10 hr |
| Specific gravity | 0.8887 ¹⁸ | 0.8703 ¹⁹ | 0.9016 ²⁴ | 0.8225 ¹⁵ |
| Refractive index | 1.4975 ¹⁸ | 1.4885 ¹⁹ | 1.4870 ²⁴ | 1.482 ¹⁵ |
| Optical rotation | +4°06' ¹⁸ | +24°22' ¹⁹ | +24°09' ²⁴ | +6°36' ¹⁵ |
| Acid value | 4.0 | 1.63 | 2.35 | 0.305 |
| Ester value | 4.4 | 6.83 | 7.05 | 0.513 |
| Ester value after acetylation | 11.7 | 43.7 | 38.9 | 73.7 |

Note : The superscripts indicate the temperature in C at which these parameters were taken.

TABLE 2. PERCENTAGE COMPOSITION OF *B. persicum* ESSENTIAL OIL FROM GILGIT, SWAT AND ZARGHOON.

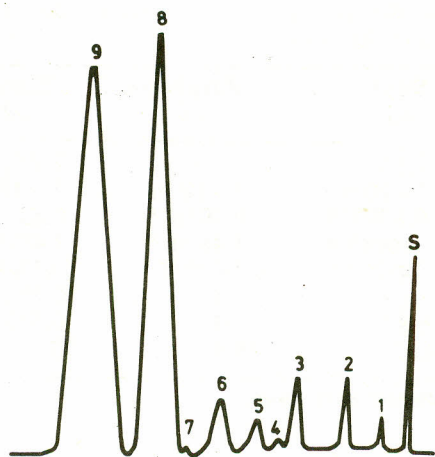
| Eluent | Constituent | Gilgit oil % | Swat oil % | Zarghoon oil % |
|-------------------------------|---------------------------------|--------------|------------|----------------|
| n-Hexane | Hydrocarbons * | 55.0 | 68.5 | 67.5 |
| | Unidentified terpene | 1.0 | — | — |
| | Unidentified terpene. | 0.1 | — | — |
| | α -pinene | — | 0.1 | 0.2 |
| | β -pinene | 1.0 | — | — |
| | Δ^3 -carene | — | 0.9 | 0.3 |
| | Limonene | 0.3 | 24.2 | 29.9 |
| | γ -terpinene | 19.8 | 28.9 | 25.0 |
| | <i>p</i> -cymene | 32.8 | 14.4 | 12.4 |
| 2% Diethyl ether in n-hexane | Cuminaldehyde | 22.5 | 17.8 | 14.8 |
| 2% Diethyl ether in n-hexane | 1,4- <i>p</i> -menthadiene-7-al | 11.2 | 3.5 | 4.2 |
| 3% Diethyl ether in n-hexane | 1,3- <i>p</i> -menthadiene-7-al | 4.8 | 5.6 | 7.2 |
| 4% Diethyl ether in n-hexane | Linalool | — | 2.0 | 0.4 |
| 10% Diethyl ether in n-hexane | Cuminyl alcohol | 3.6 | 1.0 | 5.7 |
| 20% Diethyl ether in n-hexane | Unidentified alcohols | 2.6 | 1.0 | — |
| 100% Diethyl ether | Cumic acid | 1.3 | — | — |

*Separated and estimated by GLC.

TABLE 3. PERCENTAGE COMPOSITION OF *B. persicum* ESSENTIAL OIL FROM ZIARAT.

| Eluent | Constituent | Ziarat oil % |
|-------------------------------|-----------------------|--------------|
| n-Hexane | Hydrocarbons * | 76.0 |
| | α -pinene | 2.0 |
| | β -pinene | 2.9 |
| | Δ^3 -carene | 1.8 |
| | Limonene | 3.6 |
| | β -phellandrene | 0.6 |
| | γ -terpinene | 24.0 |
| | <i>p</i> -cymene | 41.1 |
| 1% Diethyl ether in n-hexane | Myristicin | 2.0 |
| 2% Diethyl ether in n-hexane | Dillapiole | 4.0 |
| 5% Diethyl ether in n-hexane | Linalool | 16.0 |
| 6% Diethyl ether in n-hexane | Carvacrol | 1.0 |
| 20% Diethyl ether in n-hexane | Unidentified alcohols | 1.0 |

* Separated and estimated by GLC



S. Solvent, 1. Unknown, 2 α -Pinene, 3 β -Pinene, 4 Unknown, 5. Δ^3 -Carene, 6. Limonene, 7 β -Phellendrene, 8. γ -Terpinene, 9. *p*-Cymene.

Fig. 1. Gas chromatogram (obtained on a PEGS column) of the hydrocarbon fraction of Ziarat *Bunium persicum*.

position of the oil is well reflected by the variation in the composition of the essential oil of *B. persicum* obtained from the four different regions of Pakistan. (Tables 2,3). Thus, when the Ziarat, Swat and Zarghoon oils contain 76%, 68.5% and 67.5% of hydrocarbons respectively the Gilgit oil contains 55% of this fraction. Although γ -terpinene and *p*-cymene are the major terpenes in all the four oils, limonene is also one of the main terpenes in the Swat and Gilgit oils. The other minor terpenes of the hydrocarbon fraction are α -pinene, β -pinene and Δ^3 -carene of all the oils but β -phellanderene has been detected in the Ziarat oil only. In the case of the Gilgit oil, two peaks with shorter retention time than α -pinene, present upto the extent of 1.0% and 0.1% of the total oil, could not be detected. These could either be some pentene type in nature or artifacts. No sesquiterpene was detected in all the four oils.

The essential oils of Gilgit, Swat and Zarghoon contain cuminaldehyde, 1,4-*p*-menthadiene-7-al, 1,3-*p*-menthadiene-7-al and cuminyl alcohol. Cuminaldehyde was identified by comparing its IR spectrum with that reported in literature⁴ and making its 2,4-dinitrophenyl hydrazone derivative m.p. 241-243° from ethanol (lit.⁵ m.p. 243°). On reduction with lithium aluminium hydride, cuminaldehyde gave cuminyl alcohol, the IR spectrum of which matched with that of an authentic sample.

On oxidation with alkaline potassium permanganate, it gave cuminic acid m.p. 117°. 1,4-*p*-Menthadiene-7-al and 1,3-*p*-menthadiene-7-al were also identified by comparison of their IR spectra with those reported in literature.⁶

The oils from Gilgit and Swat also contained a mixture of unidentified alcohols which constituted 2.6% and 1.0% respectively of the total oils. The mixture was mainly composed of two alcohols one being primary and the other tertiary in nature. Besides these, the Gilgit oil also contains cuminic acid (1.3%) m.p. 117°, identified by IR comparison with an authentic sample. However, this acid was absent in the other three oils.

The Ziarat oil was completely devoid of aldehydes instead it contained myristicin, dillapiole, linalool and carvacrol in the oxygenated fraction. Myristicin and dillapiole were characterized and identified by IR comparison and by converting them into dibromo myristicin dibromide m.p. 128-129° (lit.⁷ m.p. 130°) and monobromo dillapiole dibromide m.p. 106-107° (lit.⁸ 107°). Linalool, one of the major components in the oxygenated fraction constituting 16% of this oil on the whole, was identified by IR comparison with an authentic sample. It was also present in Swat and Zarghoon essential oils, but its amount was only 2% and 0.4% respectively. Carvacrol, absent in the other three oils, was also identified by IR comparison.

From the above studies, it could be concluded that *B. persicum* contains two varieties of seeds which are botanically identical, but chemotaxonomically different. The seeds of *B. persicum* from Gilgit, Swat and Zarghoon are comparable with cumin seeds as a spices and yield a higher percentage of the oil.

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