

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

Part XXXIV. *Pimpinella diversifolia*, DC (Spinzankai) Seeds and Stalks Oil

MUHAMMAD ASHRAF, RAFI AHMAD and MUHAMMAD KHURSHID BHATTY

PCSIR Laboratories, Lahore

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Abstract. The percentage yield, physico-chemical values and the chemical composition of the essential oil of *Pimpinella diversifolia* seed are reported. The essential oil from the seed with a yield of 0.85% consists of santene (25.7%), α -pinene (14.4%), an unidentified monoterpene (0.7%), myrcene (15.3%), a sesquiterpene (4.0%), geranyl acetate (6.9%), carvone and pulegone (7.9%), pulegone (3.1%), α -terpineol and citronellol (2.2%), α -terpineol and terpineolic acid (6.9%) and a mixture of terpineolic acid and coumarins (7.5%). The seeds of the species possess pleasant smell and can be used as a substitute for caraway.

Introduction

The genus *Pimpinella* includes about 150 species which have been recorded to grow in Africa, Asia and South America. Only six species namely *Pimpinella acuminata*, *P. diversifolia*, *P. hazariensis*, *P. puberula*, *P. ranunculifolia* and *P. stewartii* have been reported to grow wild in Pakistan. The plants are annual or perennial herbs.

Pimpinella diversifolia is a common and a very variable species found at a height of 1500-3000 m on the hills. It grows wild in the Punjab and North West Frontier Provinces and Kashmir. The plant is used as a carminative by the local inhabitants and the seeds of the plant as a substitute of caraway. These investigations have been carried out firstly to find out the quality of the species and secondly to study the chemistry of its essential oil with a view to obtaining basic information for its use in developing new agriculture sources of such oils.

Experimental

Materials and Methods. *Pimpinella diversifolia* was collected from Ilam near Mingora (Swat) in the North West Frontier Province. The essential oil from the seeds as well as from the leaves and stalks of the species was recovered by dry steam distillation.¹ The water-soluble fraction of the oil was also extracted from the aqueous distillate with diethyl ether. Both the essential oil and the water-cobobation oil displayed identical behaviour by TLC and IR. Therefore, the two oils were mixed and the resultant oil studied for its physico-chemical values and chemical composition. The general methods employed for these studies have been reported in our earlier

publications.^{1,2}

Chromatographic Analysis of the Oil. The essential oil was resolved by column chromatography using silica gel as an adsorbent. The hydrocarbon fraction of the oil was eluted with n-hexane and the oxygenated components with an increasing preparations of diethyl ether in n-hexane. The column was finally washed with pure diethyl ether. The hydrocarbon fraction was further resolved into individual components by GLC using a 3 mm x 3 m copper column packed with 20% polyethylene glycol succinate on celite (60-80 mesh), nitrogen as the carrier gas and flame ionisation detector. The column was operated at 110°.

Results

The percentage yield, physico-chemical properties and the chemical composition of the essential oil of *Pimpinella diversifolia* are recorded in Tables 1 and 2.

TABLE 1. PERCENTAGE YIELD AND PHYSICO-CHEMICAL PROPERTIES OF THE ESSENTIAL OILS OF *Pimpinella diversifolia* SEEDS AND STALKS.

Yield and values	Oil recovered from	
	Seeds	Stalks
Distillation period	8 hr	12 hr
Yield of oil	0.85%	0.16%
Specific gravity	0.8823 ³³	0.8790 ²³
Refractive index	1.4860 ³⁵	1.4830 ²⁵
Optical rotation	+ 7° 44' ³⁵	+ 8° 12' ²⁵
Acid value	7.14	31.00
Ester value	47.00	58.00

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

TABLE 2. PERCENTAGE COMPOSITION OF THE ESSENTIAL OILS OF *Pimpinella diversifolia* SEEDS.

Components	Percentage
Santene	25.7
α -Pinene	14.4
Unidentified monoterpene	0.7
Myrcene	15.3
Limonene	4.0
Geranyl acetate	6.9
Carvone and pulegone	7.9
Pulegone	3.1
α -Terpineol and citronellol	2.2
α -Terpineol and terpinolic acid	6.9
Terpinolic acid and coumarins	7.5
Unrecovered material	5.4

Discussion

The essential oil of *Pimpinella diversifolia* possesses reasonably good smell. The oils obtained from the seeds as well as from the leaves and stalks of species is composed of identical constituents. The chemical composition of the essential oil recovered from the seeds of the species is therefore, only reported here.

The hydrocarbon fraction of the oil consisted chiefly of santene. On treatment with bromine, it yielded a tribromide m.p. 64-65° (lit.⁴ 62-63°). With hydrogen chloride, m.p. 79-81° (lit.⁴ 80°).

Besides its identification by IR comparison, the ester fraction of the oil (eluted with 2% diethyl ether in n-hexane) was hydrolysed with 0.5N alcoholic potassium hydroxide which gave geraniol by IR comparison with an authentic sample of the alcohol.

Carvone and pulegone were eluted from the column with 5% diethyl ether in n-hexane. Their R_f values were very close to each other. However, the two ketones, having conjugated double bonds, appeared fluorescent under UV light which facilitated their separation by preparative TLC. Carvone was identified by TLC, GLC and

IR comparison while pulegone by IR: (3.4, 5.9, 6.1, 7.3, 7.8, 8.8, 9.7, 10.6, 1.4 nm) and UV-absorption: $\lambda_{\text{max}}^{\text{EtOH}}$ 250 nm (lit.³ $\lambda_{\text{max}}^{\text{EtOH}}$ 252 nm).

The alcoholic fraction of the oil was eluted from the column with 10-20% diethyl ether in n-hexane. The fraction contained two alcohols, namely, α -terpineol and citronellol which were separated from each other by repeated column chromatography and identified by TLC, GLC and IR comparison with their standard samples.

Elution of the column with 50% diethyl ether in n-hexane gave a mixture of two compounds. The fraction was acidic in nature. The acidic compound was separated from the mixture by treating with saturated aqueous solution of NaHCO_3 and regenerating with dilute H_2SO_4 . The acid was identified as terpineolic acid by IR. The second compound was α -terpineol.

The last fraction was eluted from the column with 100% diethyl ether. The fraction consisted chiefly of unidentified coumarins and terpineolic acid.

The seeds of *Pimpinella diversifolia* can become a substitute for caraway. In fact, the former has since long been used as a substitute of the latter by the local inhabitants. The species has been cultivated by us in Madyan (Swat) in the North West Frontier Province and its cultivation trial at the PCSIR Laboratories, Lahore has also shown encouraging results.

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