

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

Part VII. *Psammogeton Canescens* (Khushbui) Seed Oil

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Abstract. An essential oil has been obtained in 5.8% yields by steam distillation of the seeds of *Psammogeton canescens* which is a wild growing Umbellifer of Pakistan. It is a new oil and its composition has been worked out to α -pinene (0.45%), camphene (0.73%), myrcene (0.37%), Δ^3 carene 0.36%, α -phellanderene (0.92%), limonane (58.10%), γ -terpinene (2.6%), *p*-cymene (traces), myristicin (13.2%), dillapiole (1.4%), verateraldehyde (2.0%), methyl isoeugenol (5.5%) and elimicin (11.8%). These investigations lead us to the conclusion that the oil can find application in soap, perfume and cosmetic industry.

Psammogeton canescens Boiss, synonyme *P. crinata* Boiss and *Pimpinella crinata* Boiss locally known as Khushbui grows wild in the dry, arid regions of Baluchistan. The seeds of *P. canescens* are light grey in colour, light in weight and are hairy and fluffy. Usually the plant is grazed when it is still green.

Because of the rather pleasant fruity smell of the seeds and as the plant constitutes one of the renewable resources of a relatively under developed region of Pakistan, the chemistry of its essential oil has been investigated in detail. This paper sums up the results of these investigations which are also the first ever.

Experimental

Materials and Methods. Fresh and mature seed of *P. canescens* were directly hand-collected in the Quetta region. The oil was recovered by dry steam distillation of the freshly ground seeds according to the standard method.² The instruments used in the determination of the various characteristics of the oil and the m. p. of the solid encountered in these studies have already been reported.² The chemical values of the oil were determined according to Guenther³

The essential oil was column chromatographed using silica gel as an adsorbent. The hydrocarbon fraction as eluted with n-hexane was further resolved into terpenes by GLC using 3mm \times 3m copper column packed with 7.5% carbowax on chromosorb (acid washed), nitrogen as the carrier gas and flame ionisation detector. The column temperature was maintained at 120°. The oxygenated components of the oil were identified by IR comparison and conversion into known compounds.

Results

The physicochemical values and the chemical composition of the essential oil are presented in Tables 1 and 2.

TABLE 1. PERCENTAGE YIELD AND PHYSICO-CHEMICAL VALUES OF THE ESSENTIAL OIL OF *P. canescens*.

Time of distillation	20 hi
Yield *	5.82%
Specific gravity	0.8832 ³⁵
Refractive index	1.4770 ³⁵
Optical rotation	+62°.00 ³⁵
Acid value	0.70
Ester value	10.30
Ester value after acetylation	17.70

*0.5% water-cohabation oil included. Superscripts indicate the temperature in C, at which these parameters were determined.

TABLE 2. PERCENTAGE COMPOSITION OF *P. canescens* ESSENTIAL OIL.

Eluent	Constituent	Percentage
n-Hexane	Hydrocarbons *	64.20
	Unidentified terpene	0.30
	-do-	0.37
	α -Pinene	0.45
	Camphene	0.73
	Δ^3 -Carene	0.36
	Myrcene	0.37
	-Phellandrene	0.92
	Limonene	58.10
	γ -Terpinene	2.60
2% Diethyl ether in n-hexane	<i>p</i> -Cymene	Traces
	Myristicin	13.20
2% Diethyl ether in n-hexane	Dillapiole	1.40
3% Diethyl ether in n-hexane	Verateraldehyde	2.00
4% Diethyl ether in n-hexane	Methyl isoeugenol	5.50
5% Diethyl ether in n-hexane	Elimicin	11.80
100% Diethyl ether	Mixture of coumarins (4-6)	1.80

*Resolved and estimated by GLC.

Discussion

The essential oil and the water-cohabation oil of the species displayed identical behaviour by TLC and IR; the two were, therefore, combined and the resultant material, which was pale in colour and pleasant to smell, studied for its physico-chemical characteristics and chemical composition.

The hydrocarbon fraction of the oil contained eight identifiable monoterpenes by GLC. Limonene, the most abundant single constituent in the terpenic fraction represented about 58% of the total oil. The presence of limonene to such an extent was further confirmed by the fractional distillation of the oil and the bromination of the fraction b.p. 176-178° in dry diethyl ether. A quantitative yield of limonene tetrabromide, m.p. 102-104° (lit.⁴ m.p. 105-106°) was obtained. There were two more detectable peaks (0.30, 0.37%) in the chromatogram whose retention time was shorter than α -pinene. They could either be some pentene-type in nature or artifacts. p-cymene was detected only in traces. No sesquiterpene was detected in the oil under our experimental conditions.

Fractionation of the oil through column chromatography gave myristicin (13.2%) followed by dillapiole (1.4%) with 2% diethyl ether in n-hexane. Both of these were characterised and identified by their IR comparison and making their bromo derivatives, i.e. dibromo myristicin dibromide, m.p. 128-129° (lit.⁵ m.p. 136°) and monobromodillapiole dibromide, m.p. 106-107° (lit.⁶ m.p. 107°).

Elution of the column with 3% diethyl ether in n-hexane gave verateraldehyde (2%). It was characterised by direct comparison of its IR and making its 2,4-dinitrophenyl hydrozone, m.p. 261-262° (lit.⁷ m.p. 261-263°).

Further elution of the column with 4-5% diethyl ether in n-hexane resulted in the isolation of two more phenolic ether, i.e. methyl isoeugenol (5.5%) and elimicin (11.8%). These were identified by IR comparison reported in literature^{8,9} and by making their bromo derivatives, dibromomethyl isoeugenol, m.p. 100-101° (lit.¹⁰ m.p. 101-101.5°) and dibromo elimicin, m.p. 86-88°

(lit.¹¹ m.p. 88-89°).

The oil also contained a mixture of 4-6 coumarins which are quite common constituents of the Umbelliferae family essential oils.¹²

From the above studies it can be concluded that the *P. canescens* essential oil is somewhat similar to the essential oil of *Cymbopogon* species (Gramineae family) in chemical composition. Due to its high yield and pleasant lasting odour it can be used in perfumes, cosmetics and for scenting of soaps and may prove to be a valuable commercial commodity of Pakistan.

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