Pakistan J. Sci. Ind. Res. Vol. 20, Nos. 4-5, August-October 1977

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

Part XV. Prangos pabularia ("Mushain") seed oil

MUHAMMAD ASHRAF and MUHAMMAD KHURSHID BHATTY
PCSIR Laboratories, Lahore-16

(Received February 19, 1977; revised April 4, 1977)

Abstract. The essential oil of the *Prangos pabularia* seed, with an yield 0.2%, has been examined for the first time with respect to its physico-chemical characteristics and chemical composition. The percentage composition of the essential oil is α-pinene (4.4%), camphene (traces), β-pinene (0.2%), myrcene (7.5%), Δ^3-carene (1.7%), limonene (13.64%), γ-terpinene (8.73%), β-selinene (7.3%), β-caryophyllene (3.1%), anethole (1.5%), fenchone (0.73%), unidentified esters (2.27%), cuminaldehyde (0.89%), borneol (12.8%), cumic acid (0.67%) and coumarnis (21.0%). The water cohobation oil of the species is composed of α-pinene (2.1%), camphene (1.32%), β-pinene (0.1%), myrcene (3.90%), Δ^3-carene (0.42%), limonene (6.7%), γ-terpinene (4.3%), β-selinene (5.3%), β-caryophyllene (2.52%), anethole (0.8%), fenchone (2.38%), unidentified ester (0.25%), cuminaldehyde (3.2%), α-terpineol (2.53%), unidentified alcohol (5.75%), borneol (10.82%), cumic acid (4.3%) and coumarins (40.5%).

Prangos pabularia, an umbellifer which is native to Pakistan, Afghanistan and China, resembles *Silphium parsley* of Europe, grows wild in Pakistan in the North West Frontier, Baluchistan and Azad Kashmir. The fruits of plant are employed as a winter fodder for sheep and goats. It is also considered as a reliable remedy against a dangerous disease due to *Fasciola hepatica* which often causes the death of thousands of sheep, especially after wet autumn. The flowers tops and young leaves of the plant are employed as an insect repellent in the paddy godowns by the local people.

The present studies have been undertaken for the first time to highlight the quality of the *Prangos pabularia* seed essential oil with a view to exploiting the seed or the oil commercially. This work, therefore, sums up our chemical and chromatographic investigations on the essential oil of the plant.

Materials and Methods

Mature seed of the species were collected from Chitral to recover the essential oil for these studies. The oil was recovered from the crushed seeds by dry steam distillation.[1] The general methods used for these investigations have already been described in Parts I-II of this scries.[2] The aqueous distillate was also extracted with diethyl ether and the water-cohobation oil thus obtained was studied separately.

The oil was subjected to column chromatography using silica gel as an adsorbent. The hydrocarbon fraction of the oil was resolved by GLC using nitrogen carrier gas, flame ionization detector and a copper column (3 mm×3 m) packed with 7.5% carbowax on celite (60-80 mesh) operated at 110° and 145° for the identification of monoterpenes and sesquiterpenes respectively. The oxygenated fractions containing more than one compounds were rechromatographed to obtain single components.

The chemical composition of the essential oil as well as that of the water-cohobation oil is recorded in Table 2.

Discussion

The hydrocarbon fraction of the oil was composed of both monoterpenes and sesquiterpenes. These were identified by GLC by coinjecting their standard samples. Grach[2] has shown the presence of α-pinene, myrcene and camphene in the essential oil of *P. pabularia*. But he has not reported the existence of sesquiterpene in the oil. However, Kuznetosova *et al.*[3] have reported the presence of β-caryophyllene and β-selinene in the essential oil of the *P. pabularia*.

TABLE 1. PERCENTAGE YIELD AND PHYSICO-CHEMICAL VALUES OF THE ESSENTIAL OIL OF *Prangos pabularia* SEED

Constant	Value	
	Essential oil	Water cohobation oil
Yield	0.2%	0.27%
Distillation time	8 hr.	8 hr.
Specific gravity	0.8818^{22}	0.8952^{22}
Refractive index	1.4970^{22}	1.5320^{22}
Optical rotation	$+9°30'^{22}$	$+15°15'^{22}$
Acid value	2.58	5.23
Ester value	4.30	2.58

These sesquiterpenes have also been identified in the present work (Table 2).

Results

The first oxygenated fraction of the oil was a mixture of three compounds by TLC. The fraction was rechromatographed on silica gel column employing 1-5% diethyl ether in *n*-hexane. As a result, anethole, cuminaldehyde and fenchone were separated and identified against their standard samples. Cuminaldehyde was separated by chemical method[4] from the fraction.

The next fraction when allowed to stand for a few minutes yielded a crop of crystals. The crystalline material was alcoholic in nature showing acidic properties as well. The acidic component was extracted from the mixture with sodium bicarbonate. The compound was identified as cumic acid by m.p., 115°, TLC and ir comparison. The unreacted material contained borneol which was recrystallised from ethanol and identified by m.p., 204° and ir comparison with the standard spectrum of this alcohol.

The mother-liquor from the above fraction indicated four compounds by TLC. It was, therefore, subjected to column chromatography as usual. Besides cuminaldehyde, borneol and cumic acid,

TABLE 2. PERCENTAGE OF THE ESSENTIAL OIL AND WATER-COHOBATION OIL OF *PRANGOS PABULARIA* SEED.

Solvent used	Component	Essential oil (%)	Water-cohobation oil (%)
n-Hexane	Total hydrocarbons	56.20	26.66
	α-Pinene	4.40	2.10
	Camphene	Traces	1.32
	β-Pinene	0.20	0.10
	Myrcene	7.50	3.90
	Δ^3-Carene	1.70	4.42
	Limonene	13.64	6.70
	Unidentified monoterpene	9.73	—
	γ-Terpinene	8.73	4.30
	β-Selinene	7.20	5.30
	β-Caryophyllene	3.10	2.52
2% diethyl ether in *n*-hexane	Anethole	1.50	0.80
	Fenchone	0.73	2.38
	Unidentified esters	2.27	0.25
5-20% diethyl ether in *n*-hexane	Cuminaldehyde	0.89	3.20
	α-Terpineol	1.10	2.53
	Unknown alcohol	0.98	5.75
	Borneol	12.80	10.82
	Cumic acid	0.67	4.30
50-100% diethyl ether in *n*-hexane	Bergaptene and imperatorine	—	11.70
	Mixture of coumarins	21.00	28.80
	Unrecovered material	1.86	2.81

α-terpineol were separated and identified by TLC and ir comparison. This fraction also contained an unidentified alcohol.

The last fraction was a mixture of coumarins and resinous material. Grach[2] had also reported the presence of 28% of resinous material in the essential oil of the *Prangos pabularia*. We were able to separate by preparative TLC, and identlfy imperatorin, bergaptene and osthole by m.p. and uv absorption.

The chemical composition of the essential oil of the *Prangos pabularia* seed shows that most of the constituents identified in the present work are in agreement with those which have already been reported in literature.[2,3] Besides the known constituents such as α-pinene, camphene, myrcene and borneol, however, we were able to detect and identify anethole, fenchone, cuminaldehyde, cumic acid, β-pinene Δ^3-carene and limonene in the oil but the presence of dihydrocuminol and α-phellandrene reported by earlier workers[2,3] could not be confirmed.

Acknowledgments. We are grateful to the US Department of Agriculture for financing this research and Mr. Abdul Waheed Sabir, our Botanist for the identification and procurement of the species for these studies.

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