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STUDIES ON THE ESSENTIAL OILS OF THE PAKISTANI SPECIES OF N.O. UMBELLIFERAE

Part I. *Ligusticum stewartii* (Hiroe) *E. Nasir* Seed Oil

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The essential oil of the seeds (yield 1.88%) of *Ligusticum stewartii* (Hiroe) *E. Nasir*, a wild Umbellifer of Pakistan, was analysed to total hydrocarbons (32.26%) consisting of α-pinene (8.43%), camphene (0.68%); β-pinene (3.26%); myrcene (2.84%); Δ^3-ccarene (1.67%); ρ-cymene (0.24%); limonene (8.37%); γ-terpinene (2.86%) and unknown sesquiterpenes (1.02%); a mixture (48.50%) of alcohols and esters, viz. linalool (1.56%); phenylethyl alcohol (2.31%); geraniol (6.23%); terpineol (26.14%); borniol (9.56%); bornyl acetate (1.50%); geranyl acetate (1.20%), mixture (17.3%) of coumarins and resinous materials of unknown composition and tarry matter (1.94%).

INTRODUCTION

Ligusticum stewartii (Hiroe) *E. Nasir*, is a species of the cosmopolitan plant family Umbelliferae and belongs to the genus *Ligusticum* which comprises 60 species of the perennial herbs and has specific signifiance because of its medicinal importance. Among the 60 reported species of the genus *Ligusticum*, only four species, namely, *Ligusticum stewartii L. elatum, L. marginatum* and *L. thomsonii*, occur in the Punjab, the North West Frontier Province and Kashmir in Pakistan [1].

L. stewartii (Hiroe) *E. nasir* is a wild plant and is native to Pakistan. It grows in Swat (below Kalam) and is locally called Bara-Eachga. Medicinally, it has been noted to be hypertensive, central nervous depressant and stimulant of the respiratory system. Even though the plant grows wild in large quantity in Pakistan, neither its chemistry nor the quality and chemical composition of its essential oil is known.

The present investigations have, therefore, been carried out with a view to firstly determining the chemical composition of the essential oil from its seed and then assessing its commercial importance. The results of our work have thus been reported in this communication.

MATERIALS AND METHODS

For the present studies, fresh and mature seeds of the plant were hand collected from Kalam (Swat) in the North West Frontier Province. The essential oil was recovered from the crushed seeds by dry steam distillation. The water immiscible part of the essential oil was collected using a separatory funnel while the miscible fraction obtained by three successive extractions of the distillate with diethyl ether. The extractions were combined and freed from water by treatment with anhydrous sodium sulphate. The solvent was carefully removed at low temperature and the residue combined with the water immiscible fraction thus yielding 1.88% of the oil. The physico-chemical evaluation of the oil was carried out according to the methods already given in our earlier papers [3-4] and the results have been tabulated (Table 1).

The essential oil was resolved into different fractions by column chromatography using silica gel as an adsorbent. The solvent scheme used for the elution of the various fractions from the column is shown in Table 2. Gas Liquid chromatographic analysis of the fractions was carried out on a Pye-Unicam 104 Gas chromatograph fitted with a flame ionisation detector using a 25 m Wcot SP-1000 column. Hydrogen was used as the carrier gas with a flow rate of 67.75 cm/sec and split ratio of 1:60 and sample size 0.1 μl. The temperature was programmed as 50° for 3 min with 10°/min increase to 100°, detector temperature 250° and injection temperature 200°. The results are given in Table 3.

RESULTS AND DISCUSSION

The essential oil of *L. stewartii* is remarkably sweet smelling. Its physico-chemical parameters are shown in

Table 1. These values are comparable to the reported values for the other species of the genus *Ligusticum* [5]. Table 2 shows the resolution of the oil in polar and non-polar solvents over silica gel into hydrocarbons, oxygenated compounds and tarry matter. The oil contains 32.26% hydrocarbons. GLC analysis as given in Table 3 shows the usual pattern of monoterpenes as reported in the literature [6, 7] for the other species of the genus *Ligusticum*. However, the sesquiterpenes are still under investigation.

The predominent fraction of the essential oil consists of the oxygenated compounds, viz. acetates, alcohols and coumarins. The first two fractions of the oxygenated compounds which are the esters, were hydrolysed with 0.5N alcoholic potassium hydroxide and the alcohols isolated and identified by TLC and GLC as geraniol and borneol. The acid portion was identified as acetic acid by its characteristic reactions which indicated the presence of acetates of geraniol and borneol in the essential oil of *Ligusticum stewartii*. The other exygenated components of the oil as eluted from the column were identified as α-terpineol, geraniol, borneol, linalool and phenylethyl alcohol, by preparative TLC and ir analysis of the individual components.

Table 1. Physico-chemical characteristic of the essential oil of *L. stewartii* (Hiroe) *E. Nasir* Seeds

Oil yield	1.88% (10 hrs distillation)
Specific gravity	0.9101^{24}*
Refractive index	1.5027^{24}*
Optical rotation	$+14^{o} - 22'$
Acid value	16.44
Ester value	2.44

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

Table 2. Fractionation of *Ligusticum stewartii* (Hiroe) *E. Nasir* essential oil.

Fraction No.	Solvent System	Volume (ml)	Quantity obtained(g)
1.	η-Hexane	120	3.226
2.	η-Hexane	80	
3.	Diethylether 2% in hexane	120	0.270
4.	Diethylether 5% in hexane	120	4.580
5.	Diethylether 10% in hexane	120	
6.	Diethylether 100%	80	1.730
7.	5-10% ethanol in diethylether	120	0.194

Table 3. Percentage composition of the essential oil of *Ligusticum stewartii* (Hiroe) *E. Nasir*

Component	Percentage
Hydrocarbons	
α-Pinene	8.43
Camphene	0.68
β-Pinene	3.26
Myrcene	2.84
Δ^3-Carene	1.67
ρ-Cymene	0.24
Limonene	8.37
α-Terpinene	2.86
Unknown sesquiterpenes	1.02
Oxygenated	
Geranyl acetate	1.20
Bornyl acetate	1.50
α-Terpineol	26.14
Geraniol	6.23
Borneol	9.56
Linalool	1.56
Phenylethyl alcohol	2.31
Mixture of coumarins and resinous material	17.31
Tarry matter	1.94

A large amount of coumarins and resinous material was also eluted. Work on the identification of coumrins is in progress. The tarry matter, obtained by washing out the column with alcohol, remains to be resolved.

The chemical composition of the essential oil of the *Ligusticum stewartii* (Hiroe) *E. Nasir* seeds (Table 3) indicates that the oxygenated components like terpineol, geraneol, linalool and borneol, occupying a unique position in perfumery, are the major components of the seential oil and thus impart a sweet smell to the oil. It has, therefore, been concluded that the essential oil of *Ligusticum stewartii* can be utilized for commercial purposes, provided the plant species is tamed for cultivation.

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