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

Part XII. Ligusticum thomsonii ("Dugzira") seed oil

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Abstract. The essential oil distilled from the seed of *Ligusticum thomsonii*, growing wild in Pakistan, has been physico-chemically characterized and studied for its chemical composition. It consists of thujene (0.31%), α-pinene (0.58%), camphene (0.74%), myrcene (1.77%), Δ^3-carene (1.46%), β-phellandrene (1.54%) limonene (2.15%), α-phellandrene (1.44%), γ-terpinene (1.18%), unidentified sesquiterpenes (1.93%), β-selinene (0.90%), linalyl acetate (0.89%), geranyl acetate (0.41%), α-terpineol (26.4%), mixture of terpineol and borneol (8.62%), coumarins (35.84%) and tarry material (4.66%).

Ligusticum is a genus of over 60 species and is well represented in the Himalayas from 2000-3000 m. above the sea level. Only four species, including *Ligusticum thomsonii*, have been reported so far to grow in Pakistan.

L. thomsonii, a wild umbellifer is native to Pakistan, Afghanistan and China.[1] Its essential oil indicates hypotensive, central nervous depressant and smooth muscle relaxant effects. On the basis of its sweet smell the essential oil can find application in perfumery as well.

Although the plant grows in large quantity in Pakistan as a wild species, the quality and chemical composition of the essential oil of its seed are not known. The present investigations have, therefore, been carried out with a view to evaluating its commercial importance with particular reference to the chemical composition of the essential oil from its seed and the results of work have been summed up in this communication.

Materials and Methods

Mature seeds of the plant were collected from Kaghan in the North West Frontier Province. As usual, the essential oil from the crushed seeds was recovered by dry steam distillation[2]. Both the essential oil and water cohobation oil (0.21%) displayed identical behaviour by TLC and ir. They were combined and the oil thus obtained was studied for its physico-chemical properties and chemical composition. The instruments used for the determination of physical constants (Table 1) of the oil have been described earlier.[2] A Beckman DB spectrophotometer was used to record uv spectra. Chemical values of the oil were determined according to Guenther[3] (Table 1).

The essential oil was subjected to fractionation by column chromatography using silica gel as an adsorbent. The solvents used for the elution of the various fractions from the column are indicated in Table 2. The oxygenated fractions constituting more than one component were rechromatographed for single compounds and studied by TLC, ir, uv, GLC, etc. for identification. The hydrocarbon fraction was resolved into individual components 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 150° for monoterpenes and sesquiterpenes respectively.

The chemical composition of the essential oil is recorded in Table 2.

Results

TABLE 1. PHYSICO-CHEMICAL CONSTANTS OF THE ESSENTIAL OIL OF *LIGUSTICUM THOMSONII* SEED.

Constant	Value
Specific gravity	0.9931^{27}
Refractive index	1.4870^{27}
Optical rotation	$+19°\ 10'^{27}$
Acid value	14.51
Ester value	32.24
Ester value after acetylation	93.20

Discussion

The major fraction of the essential oil is predominantly composed of oxygenated compounds, *viz.*, acetates, alcohols and coumarins. The first oxygenated fraction on elution with 2% diethyl ether in *n*-hexane gave a single compound whose ir was

TABLE 2. PERCENTAGE COMPOSITION OF THE ESSENTIAL OIL OF *LIGUSTICUM THOMSONII* SEED.

Solvent used	Component	Percentage
	Total hydrocarbons	14.09
n-Hexane	α-Thujene	0.31
	α-Pinene	0.58
	Camphene	0.74
	Myrcene	1.77
	$\triangle^3$-Carene	1.46
	α-Phellandrene	1.54
	Limonene	2.15
	β-Phellandrene	1.44
	γ-Terpinene	1.18
	Unknown sesquiterpinene	0.81
	,,	1.21
	β-Selinene	0.90
2% diethyl ether in *n*-hexane	Linalyl acetate	0.89
2-5% diethyl ether in *n*-hexane	Geranyl acetate	0.41
5-10% diethyl ether in *n*-hexane	α-Terpineol	26.40
	α-Terpineol and borneol	8.62
100% diethyl ether	Mixture of coumarins and resinous material	35.84
5% ethanol in diethyl ether	Tarry material	9.66
	Unrecovered material	4.09

identical with that of linalyl acetate. On hydrolysis with 0.5N alcoholic KOH, linalool as identified by TLC and ir was obtained. The acid regenerated from the potassium salt gave typical reactions of acetic acid. Further elution of the column gave two esters, linalyl and geranyl acetates by TLC and ir examination.

The major oxygenated component of the oil, as eluted from the column, was identified as α-terpineol by TLC and ir examination.

The essential oil contained a large amount of coumarins and tarry material. The major coumarin was separated from the mixture by means of preparative TLC. Its uv spectrum gave maximum absorption at λ^{EtOH}_{max}. 278 μm. But further work is needed to identify the coumarin.

The chemical composition of the essential oil of the *Ligusticum thomsonii* seed (Table 2) indicates that α-terpineol, a cyclic terpene alcohol enjoying unique position in perfumery, is the major constituent of the oil. The oil of the species, therefore, can be utilized for industrial purposes, provided the plant is tamed by cultivation. Our results in this direction are quite encouraging.

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