

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

Part XXII. *Ferula foetida* Regel (Ushi) Seed Oil

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Abstract. The essential oil from the fresh mature seed of the *Ferula foetida* Regel, grown in Pakistan, has been examined with respect to its physico-chemical characteristics and chemical composition. The percentage composition of the oil as determined by column chromatography coupled with gas-liquid chromatography of the hydrocarbons and physico-chemical investigation of the oxygenated components is reported. Its final composition, as determined by this method as well as from the time and temperature programmed GLC/MS studies of the alcoholic fraction is: α -pinene (2.36, 1.69%), camphene (1.04, 0.90%), myrcene (2.50, 2.00%), limonene (0.60, 0.72), unknown sesquiterpene (1.00, 0.72%), longifolene (5.90, 4.60%), cadinene (0.90, 0.30%), β -caryophyllene (5.00, 3.80%), β -selinene (17.20, 15.20%), unknown sesquiterpene (1.40, 1.00%), bornyl acetate, (2.25, 4.50%), fenchone (1.50, 2.40%), eugenol (5.00, 4.68%), linalool (0.06, 0.05%), geraniol (0.05, 0.08%), isoborneol (0.0, 0.4%), borneol (0.15, 0%), guaiaol (0.9, 57%), cadinol (0.17, 90%), farnesol (0.13, 07%), mixture of sesquiterpenic alcohols (39.32, 0%) and a mixture of coumarins (7.50, 7.80%). The presence of sulphur bearing compounds was not detected in the oil.

Introduction

Ferula foetida is native to Pakistan, Afghanistan and Iran. In Pakistan, it grows profusely in different places in Baluchistan and the North West Frontier Province.¹ The plant gum, a resin obtained from the stems of the plant, called *Ferula assafoetida* ("hing") is a traditional flavouring agent and is regarded as an ingredient of species. Its medicinal uses are many and well known.²

According to the earlier reports² *F. foetida* has been studied either as a whole plant or its gum which has been investigated in detail. No work has been reported so far on the essential oil of the seed of this plant. The present studies, therefore, have been undertaken to determine the physico-chemical properties and the chemical composition of the essential oil of the seed to obtain basic information upon the nature and possible commercialisation of this oil.

Experimental

Materials. Fresh *F. foetida* seeds were used for these studies. The essential oil from the crushed seeds was recovered by dry steam distillation.⁴ The general methods employed for this work have been described in our earlier publications.⁴ Activated silica gel was used for column chromatography.

Hydrocarbon fraction of the oil, as eluted from the column with *n*-hexane, was analyzed by GLC using copper column (3 mm \times 3 m) packed with 20% polyethylene glycol succinate on Celite (60-80 mesh), nitrogen as carrier gas and flame ionization detector. The column temperature was maintained at 120 and 170° for the resolution of monoterpenes and sesquiterpenes respectively. The oxygenated components of the oil were identified by TLC, ir and GLC comparison with their authentic samples. However, in order to have the oil examined rather minutely with the most up to date and advanced techniques, the alcoholic fraction of the oil was also analyzed by time and temperature programmed GLC/MS employing 0.25" \times 6' glass column packed with 3% Silar 5 cp and identified the various components of the oil from the computerized results of GLC chromatogram and mass spectra.

Results

The percentage yield, physico-chemical properties and the chemical composition of the essential oil as determined by column chromatography/GLC and GLC/MS are recorded in Tables 1 - 2. Fig. 1 shows the resolution of the alcoholic fraction, obtained from the column, by time and temperature programmed GLC.

TABLE 1. PERCENTAGE YIELD AND PHYSICO-CHEMICAL PROPERTIES OF THE ESSENTIAL OIL OF *F. foetida* SEED.

Distillation time	10 hr
Yield	3.0%
Specific gravity	0.9500 ²⁰
Refractive index	1.4950 ²⁵
Optical rotation	-31°34' ²²
Acid value	7.45
Ester value	12.65

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

TABLE 2. PERCENTAGE COMPOSITION OF THE ESSENTIAL OIL OF *F. foetida* SEED BY COLUMN/GLC AND GLC/MS.

Eluents	Component	Percentage by	
		Column/ GLC	GLC/MS
<i>n</i> -Hexane	Hydrocarbons	39.90	31.02
	α -Pinene	2.36	1.69
	Camphene	1.04	0.90
	Myrcene	2.50	2.00
	Limonene	0.60	0.72
	Unknown ses- quiterpene	1.00	0.82
	Longifolene	5.90	4.60
	Cadinene	0.90	0.30
	β -Caryophyllene	5.00	3.80
	β -Selinene	17.20	15.20

2% diethyl ether in <i>n</i> -hexane	Unknown ses- quiterpene	1.40	1.00
	Bornyl acetate	2.25	4.50
	Fenchone	1.50	2.40
10-15% diethyl ether in <i>n</i> -hexane	Eugenol	5.00	4.68
	Alcoholic frac- tion	50.13 ^a	52.07 ^b
5-10% diethyl ether in <i>n</i> - hexane	Linalol	0.06	0.05
	Geraniol	0.05	0.08
	Isoborneol	—	0.04
	Borneol	0.15	—
	α -Terpineol	0.85	0.98
	Unknown alcohol	1.30	1.60
	-do-	0.90	0.98
20-50% diethyl ether in <i>n</i> - hexane	Guaicol ^c		9.57
	Cadinol	39.32	17.90
	Farnesol		13.07
5% ethanol in diethyl ether	Coumarins	7.50	7.80
	Unrecovered material	3.22	5.32

(a) Resolved and estimated by GLC.

(b) Resolved and estimated by time and temperature programmed GLC/MS.

(c) Not resolved under the conditions.

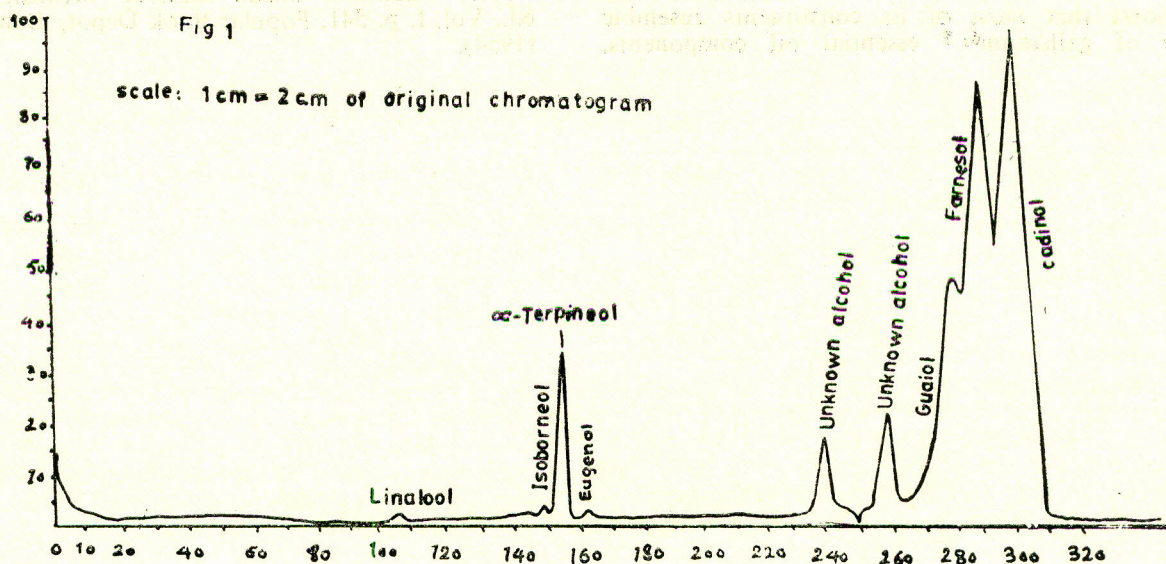


Fig. Time temperature programmed GLC of *Ferula foetida* alcoholic fraction using 3% silar 5cp column (0.25" x 6')

Discussion

The essential oil the *F. foetida* possess a fairly pleasant smell but a bitter taste. The deterpinated oil is chiefly composed of sesquiterpenic alcohols which are pleasant to smell.

Storage of the seed materially affects the yield and the composition of the oil. Thus, when the seeds had been stored for more than six months, the yield of the oil had decreased by 33% with the amount of hydrocarbons reduced by about 7% in the meanwhile. This phenomenon had, however, resulted in an overall increase in the oxygenated components, particularly the alcoholic content of the oil.

The hydrocarbon fraction of the oil consisted of mono- and sesquiterpenes, both being identified by GLC against their standard samples. The monoterpenes were also separated from the sesquiterpenes by fractional distillation at 120°. The residual sesquiterpenes turned blue at this temperature, thus indicating the presence of sesquiterpenes or some that are the precursors to azulenes.⁵

The oxygenated fraction consisted mainly of saturated sesquiterpenic alcohols which are tertiary in nature as shown by the chemical tests. The alcohols could not be resolved by means of column chromatography into individual constituents. Their identification and estimation were carried out by GLC. Identification of guaial is tentative depending solely upon the GLC/MS data.

The last oxygenated fraction, as washed out from the column with diethyl ether and ethanol mixture, appeared fluorescent under uv light. The fraction was acidic in reaction and its IR spectrum indicated the presence of ferulic acid.

The chemical composition of the *F. foetida* essential oil shows that most of its constituents resemble those of galbanum^{6, 7} essential oil components.

The oil from *F. foetida* could, therefore, become a reasonably good substitute for galbanum essential oil which finds application in various diseases.⁸

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