Technology Section

Pakistan J. Sci. Ind. Res., Vol. 22, No. 6, December 1979

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

Part XXXV. *Ferula assafoetida* Linn. (Hing) Seed Oil

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(Received June 10, 1979)

Physicochemical investigations on the essential oil from the fresh seeds of *Ferula assafoetida* have been carried out for the first time with a view to exploiting the indigenous raw material of the country. The essential oil with an 1.5% yield is constituted of ∝-pinene (1.43%), phellandrene (5.48%), an unidentified monoterpene (2.99%), secondary butyl propenyl disulphide (35.12%), geranyl acetate (7.71%) bornyl acetate (9.33%), ∝-terpineol (12.71%), a mixture of ∝-terpineol and an unknown alcohol (2.10%), myristic acid (21.23%) and a mixture of coumarins (1.90%). Secondary butyl propenyl disulphide, the major constituent of the oil, is attributed to the characteristic smell of the essential oil.

INTRODUCTION

Ferula is the largest genus in the Umbelliferae family consisting of 140 species spread from the Mediterranean region to Central Asia. The highest concentration of the species is met with in the USSR and adjacent regions. Only 15 species have so far been reported to occur in Pakistan. These species are: *Ferula assafoetida, F. baluchistanica, F. communis, F. foetida, F. hindukushensis, F. jaeschkeana, F. kokanica, F. lehmannii, F. microlobs, F. narthex, F. oopoda, F. ovina, F. reppiae, F. rubicaulis* and *F. stewartiana.* The plants are perennial herbs.

Ferula assafoetida is a native to Afghanistan and Iran. The young raw cabbage-like tops of the plant are used by the local inhabitants as salad. The plant exudes a gum which finds wide applications in flavouring various kinds of food products and also as a medicine [1, 2]. The gum has also been recommended in pharmaceutical preparations as a local stimulant to the mucous membrane of alimentary canal. We have also shown that the essential oil obtained from the seed of the plant is quite effective against *Staphylococcus aurius* and *Streptococcus foecalis.*

The present studies have been carried out to evaluate the quality and chemical composition of the essential oil of the seeds of *F. assafoetida* to obtain basic information for use in developing new agricultural sources of such oils. This communication, therefore, sums up the results of our work on the essential oil of the seed of *F. assafoetida* grown in Pakistan.

MATERIALS AND METHODS

Mature seeds of the *F. assafoetida* were collected from Baluchistan. The essential oil from the crushed seeds was recovered by dry steam distillation [3]. The general methods used for analysis of the oil have already been reported in our earlier papers [3, 4].

The details of the procedure used for chromatographic analysis of essential oils have been described in our earlier work [3, 4]. Briefly, a weighed quantity of the oil (5 g) was loaded on a glass column (100 x 3.5 cm) packed with activated silica gel (150 g). The hydrocarbon fraction of the oil was eluted from the column with n-hexane. The fraction was further resolved into individual components by GLC using a copper column (3 m x 3 mm) packed with 7.5% carbowax on Celite (60–80 mesh), nitrogen as the carrier gas and flame ionisation detector. The column temperature was maintained at 110 and 170° for the resolution of monoterpenes and sesquiterpenes respectively. The oxygenated components were eluted from the column with 1–50% diethyl ether in n-hexane and finally the column was washed with 100% diethyl ether. The oxygenated components of the oil were identified by m.p. TLC, GLC and IR comparison method.

RESULTS

The percentage yield of the oil, its physicochemical values and chemical composition are recorded in Tables 1

Table 1. Percentage yield and physicochemical values of the essential oil of *Ferula assafoetida* seeds

Distillation period (hr)	14
Yield of oil (%)	1.5% including water cohobation oil
Specific gravity	0.8605^{30}
Refractive index	1.5270^{30}
Optical rotation	$34^{o\ 30}$
Acid value	22.0
Ester value	31.0

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

Table 2. Percentage composition of the essential oil of *Ferula assafoetida* seeds.

Eluent	Constituent	Percentage
n-Hexane	Hydrocarbons*	9.90
	α-Pinene	1.43
	Phellandrene	5.48
	Unknown monoterpene	2.99
2% Diethyl ether in n-hexane	Secondary butyl propenyl disulphide	35.12
4% Diethyl ether in n-hexane	Geranyl acetate	7.71
-do-	Bornyl acetate	9.33
10% Diethyl ether in n-hexane	α-Terpineol	12.71
-do-	Mixture of α-terpineol and unknown alcohol	2.10
30% Diethyl ether in n-hexane	Myristic acid	21.23
50% Diethyl ether in n-hexane	Mixture of coumarins and tarry material	1.90

*Resolved and estimated by GLC

and 2.

DISCUSSION

The essential oil obtained from the seeds of *Ferula assafoetida* is brownish in colour and possesses a garlic-like smell. Besides the high percentage of sulphur, as determined by the sulphur element tests, the higher acid and ester values of the oil indicate the presence of a considerable amount of oxygenated compounds.

The hydrocarbon fraction of the oil contains three monoterpenes while no sesquiterpene is detected (Table.2). The essential oil of the *F. assafoetida* seed, as shown by the present studies is chiefly composed of secondary butyl propenyl disulphide, geranyl acetate, bornyl acetate, α-terpineol and myristic acid. All these compounds, except for secondary butyl propenyl disulphide have not been reported earlier to be present in the essential oil of the gum of this species and are considered to be a new finding in the essential oil of the *F. assafoetida* seed. These oxygenated compounds have been reported to be the constituents of the essential oils recovered from the seeds of other *Ferula* species [5] which, however, do not contain any sulphur-bearing compounds. The presence of sulphur bearing compound in the essential oil recovered from the seed of *F. assafoetida* alongwith the above cited constituents gives this oil a position which serves as a bridge between the essential oil of the gum of this species and the seed essential oil of other *Ferula* species such as *F. costata, F. foetida, F. narthex F. oopoda* and *F. ovina.*

Secondary butyl propenyl disulphide was identified by TLC and IR (3.4, 6.3, 7.0, 7.3, 8.5, 9.6, 9.9, 10.1, 10.8, 11.2, 13.2, 14.3 nm) comparison with the standard sample obtained from the gum of *F. assafoetida*. It is this compound to which the characteristic smell of the essential oil can mainly be attributed to.

Geranyl and bornyl acetates were identified by TLC, IR and GLC comparison method. The esters were also hydrolyzed with 0.1*N* alcoholic KOH to their parent alcohols and identified by IR comparison with the standard spectra of these compounds.

α-Terpineol, which was eluted from the column with 10% diethyl ether in n-hexane, was identified by TLC and IR comparison with its standard sample.

The column when eluted with 30% diethyl ether in n-hexane gave a single compound by TLC. On removal of the solvent the fraction changed into crystalline form. The compound was identified as myristic acid by m.p. 53^{o} and IR: (3.1, 3.2, 5.9, 6.7, 7.0, 7.1, 7.8, 8.3, 9.2, 9.8, 10.8, 13.9 nm) comparison with the standard spectrum of the compound.

The present studies indicate that the essential oils obtained from the seeds of *F. assafoetida* and that of its gum have identical constituents and, therefore, the former can be used as a flavouring agent and also in medicine. In addition the essential oil of the *F. assafoetida* seed possesses good smell due the presence of esters and cyclic terpenic alcohol.

Acknowledgements. We are grateful to the United States Department of Agriculture for financing this research under a PL-480 scheme and to Mr. Abdul Waheed Sabir, our Botanist, for the identification and procurement of authentic samples for these studies.

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