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

Part. XXVI - *Ferula oopoda*, Boiss Buhse (Chir) oil from the Seeds, Stalks and Roots

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The essential oils from the various parts of the plant of *Ferula oopoda* have been studied for their physicochemical properties and chemical composition. The oil obtained from the mature seed (3.7%), immature seed collected on two dates (2.3, 5.0%), leaves and stalks (1.32%) and roots (1.15%) have shown to respectively contain α-pinene (1.2, 0.5, 0.3, traces, 0.1%), β-pinene (0.4, 0.2, 0.1, traces, 0.1%), myrcene (30.3, 34.4, 31.5, 0.1, 1.3%), limonene (28.8, 22.3, 26.3, 0.2, 2.1%) *p*-cymene (3.9, 5.2, 6.5, 0.1, 0.4%), β-elemene (1.3, traces, traces, 0.4, 0.7%), an unknown sesquiterpene (1.2, traces, 0.9, 0.3, 0.5%), β-caryophyllene (3.7, 3.2, 3.3, 0.3, 3.6%), humulene (2.7, 2.0, 2.4, 0.6, 2.0%), β-selinene (3.3, 4.2, 2.8, 0.8, 0.8, 2.2%), methyl thymol (5.2, 2.6, 3.3, 0.9, 41.2%), a mixture of unknown compounds (1.3, 1.2, 2.4, 8.8, 0.4%), myristicin (4.4, 1.7, 2.2, 0.8, 11.2%), fenchone and α-terpineol (0.0, 2.6, 3.1, 0.6, 3.4%), α-terpineol and geraniol (5.0, 2.6, 4.0, 0.0, 0.0%) and a crystalline lactone compound (2.4, 9.6, 2.9, 61.0, 23.3%).

The plant has been investigated for the first time in respect of its essential oil which is present in all parts of the species and of which the highest amounts have been distilled from the immature seed. However, the oil of the various parts of the plant is pleasant to smell.

INTRODUCTION

Ferula oopoda is a wild plant and is distributed to Pakistan, Iran and Russia. In Pakistan, it grows in the Baluchistan region. The seeds of the species are stimulant, carminative, antispasmodic, laxative and diuretic.

Although large quantities of *Ferula oopoda* grow in Pakistan, yet the quality and chemical composition of its essential oil have not been studied. The present work was, therefore, carried out to evaluate the commercial importance of the species.

EXPERIMENTAL

Materials and Methods

The plant of *Ferula oopoda* with mature seeds, immature seeds and also its roots were hand-collected from Baluchistan for these studies. The oil from various parts of the species was steam-distilled according to the standard procedure [1]. The essential oils obtained from different parts of the species were studied separately. The general methods employed for the analysis of the oils have been described in our earlier publications [1,2]. NMR was used for the structure determination of the solid major ketonic compound present in the oil.

Chromatographic Analysis of the Oil. The essential oil obtained either from the seeds or leaves and stalks or the roots of the species was fractionated into hydrocarbons and oxygenated components using silica gel chromatography and different systems of solvents starting from n-hexane for the elution of hydrocarbons followed by 0.1–20% diethyl ether in n-hexane for the majority of oxygenated components.

The hydrocarbon fraction was further resolved by GLC using a copper column (3m × 3mm) packed with 20% polyethylene glycol succinate, nitrogen as the carrier gas and flame ionisation detector. The temperature of the column was maintained at 110° and 175° for the resolution of monoterpenes and sesquiterpenes respectively. The hydrocarbon components of the oil were identified against their standard samples.

The oxygenated components of the oil were identified by TLC, IR, GLC and by preparing their known derivatives.

RESULTS

The percentage yield, physicochemical properties and the chemcial composition of the essential oils recovered from the various parts of *Ferula oopoda* are recorded in Tables 1 and 2.

DISCUSSION

The maximum yield of the essential oil of *Ferula oopoda* at different stages of growth was obtained from its immature seed. Besides the seeds, the other parts of the plant, i.e. roots and leaves and stalks at the stage of maturation also contain considerable amount of essential oil which is mainly composed of oxygenated compounds.

Elution of the column with n-hexane gave a hydrocarbon fraction amounting to 72–78% in the seed essential oil, 13% in the roots and 2.8% in the leaves and stalks essential oil. A detailed sltudy of the individual monoterpenes and sesquiterpenes in each of the hydrocarbon fraction was carried out by GLC.

The column when eluted with 0.1% diethyl ether in n-hexane gave a single compound by TLC. It was identified as methyl thymol by IR: (3.4, 6.2, 6.3, 6.7, 6.9, 7.1, 8.0, 8.6, 9.1, 9.7, 10.8, 12.2 nm) comparison with an authentic sample which was prepared by treating thymol with methyl iodide and anhydrous sodium carbonate. Elution of the column with 0.2% diethyl ether in n-hexane gave a mixture of three compounds. One of these compounds was methyl thymol as separated by rechromatography and identified by TLC and IR. The second compound was a crystalline solid and third a flourescent liquid. Their further separation and identification have not been attempted as yet.

Elution of the column with 0.5% diethyl ether in n-hexane gave a mixture of two compounds by TLC. The mixture was resolved into hydroxy and phenolic ether components. The phenolic ether compound was identified as myristicin by IR. On treatment with bromine in dry ether, it gave tetrabromide, m.p.127 – 28° (lit [3] 130°). The second compound was identified as α-terpineol by IR comparison.

Further elution of the column with 1% diethyl ether in n-hexane gave a mixture of two compounds by TLC and were ketonic and hydroxy by IR. This fraction was, however, absent in the mature seed essential oil. The compounds were α-terpineol and fenchone.

The column was then eluted with 10% diethyl ether in n-hexane which gave a single crystalline compound by TLC and IR: (3.3, 3.4, 5.8, 6.1, 6.8, 7.3, 8.5, 9.8, 10.1, 10.2, 11.2, 12.5, 13.4, 15.0 nm). It was one of the main components in the leaves and stalks essential oil (61.0%). It was present to the extent of 23.3% in the roots and 2.9–9.6% in the seed essential oil.

The mol wt of the ketonic compound is 232 by mass spectrometery. From proton and carbon NMR spectra, the formula which fits is $C_{15}H_{20}O_2$ and this is confirmed by elemental analysis. Its proton spectrum is as follows:

($CDCl_3$)

δ 1.12 (d, 3H) CH_3 –C H ; δ 1.66 (t, 2H) CH_2
δ 1.80 (m, 3H) CH_3 –C=C ; δ 2.40 (t, 4H) CH_2,CH_2
δ 2.70 (m, 3H) C*H*,C*H*,C*H* ; δ 3.04 (m, 1H) C*H*
δ 4.29 (m, 1H) C*H* ; δ 4.78 (m, 2H) =CH_2
δ 5.43 (m, 1H), C*H*

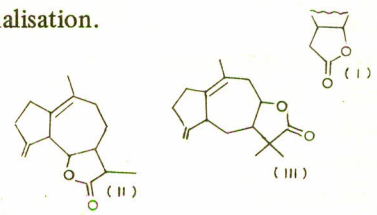
The position of the terminal olefin protons indicates that it is probably an exocyclic methylene.

The carbon NMR of the compound is as follows:

($CDCl_3$)

δ 179.1	s	$C=O$	;	δ 147.7	s	$C=C$
δ 143.0	s	$C=C$	;	δ 125.5	d	$H-C=C$
δ 111.9	t	$C=C$	;	δ 84.3	d	$C-O$
δ 52.1	d	$C-H$	;	δ 47.7	d	$C-H$
δ 38.9	d	$C-H$	;	δ 37.8	d	$C-H$
δ 34.7	t	CH_2	;	δ 33.9	t	CH_2
δ 19.6	t	CH_2	;	δ 17.3	q	$CH_2-C=$
δ 11.0	q	CH_3				

The position of the carbonyl indicates that it may be part of a γ-lactone (I). On the basis of the available data the proposed structure of the compound is either (II) or (III). The validity of the either of the two structures, however, still awaits finalisation.



Finally, the column was eluted with 20% diethyl ether in n-hexane which gave another single ketonic compound by TLC and IR: (3.3, 3.4, 5.8, 6.0, 6.9, 7.5, 8.1, 9.1, 9.8, 11.2, 12.4, 13.2, 13.8, 15.0 nm). It was a liquid and seemed to be a lactone in nature.

The essential oil of *Ferula oopoda* seems to be a good substitute of Galbanum essential oil. The oil of the various parts of the plant is pleasant to smell.

Table 1. Percentage yield and physicochemical values of the essential oil obtained from the different parts of *Ferula oopoda*.

Yield and value	Oil recovered from				
	Mature seed	Immature seed collected on		Leaves and stalks	Roots
		9.5.1974	23.5.1974		
Distillation time (hr)	14	24		32	20
Yield of oil (%)	3.7	2.3	5.0	1.32	1.15
Specific gravity	0.8041^{15}	0.8002^{32}	0.8169^{32}	1.0010^{32}	0.9292^{32}
Refractive index	1.4840^{15}	1.4800^{32}	1.4790^{32}	1.5210^{32}	1.5040^{32}
Optical rotation	$-6^{o}28'^{15}$	$-14^{o}\ 0'^{32}$	$-10^{o}\ 51'^{32}$	$-97^{o}\ 39'^{32}$	$-16^{o}\ 48'^{32}$
Acid value	0.12	0.61	0.51	6.50	0.72
Ester value	9.79	39.08	32.30	171.31	40.65
Ester value after acetylation	75.53	76.57	64.57	195.82	80.10

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

Table 2. Percentage composition of the essential oil obtained from different parts of *Ferula oopoda*.

Component	Oil recovered from				
	Mature seed	Immature seed collected on		Leaves and stalks	Roots
		9.5.74	23.5.74		
	(%)	(%)	(%)	(%)	(%)
α-Pinene	1.2	0.5	0.3	Traces	0.1
β-Pinene	0.4	0.2	0.1	Traces	0.1
Myrcene	30.3	34.4	31.5	0.1	1.3
Limonene	28.8	22.3	26.3	0.2	2.1
p-Cymene	3.9	5.2	6.5	0.1	0.4
β-Elemene	1.3	Traces	Traces	0.4	0.7
Unknown sesquiterpene	1.2	Traces	0.9	0.3	0.5
β-Caryophyllene	3.7	3.2	3.3	0.3	3.6
Humulene	2.7	2.0	2.4	0.6	2.0
β-Seilenene	3.3	4.2	2.8	0.8	2.2
Methyl thymol	5.2	2.6	3.3	0.9	41.2
Mixture of unknown compounds	1.3	1.2	2.4	8.8	0.4
Myristicin	4.4	1.7	2.2	0.8	11.2
Fenchone and α-terpineol	-	2.6	3.1	0.8	3.4
α-Terpineol and geraniol	5.0	2.6	4.0	-	-
Lactone (Solid)	2.9	9.6	2.9	61.0	23.3
Lactone, low m.p.	4.4	7.2	8.4	25.1	7.5

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