

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

Part XLIV. *Selinum candollei*, DC (Theem) Seed Oil

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The essential oil steam-distilled from the seed of *Selinum candollei* has been characterised and studied for its physicochemical properties and chemical composition. The oil obtained in 1.5% yield is composed of 2,3-dimethyl-3-ethyl pentane (0.24%), α -thujene (0.20%), α -pinene (0.69%), phenyl methyl ketone (0.08%), santene (0.12%), 1-methyl-4-isopropenyl benzene (0.12%), salinene (1.04%), 2, 4-dimethyl hexane (0.03%), β -pinene (0.57%), myrcene (3.88%), n-undecane (1.88%), γ -terpinene (0.25%), *p*-cymene (9.00%), Δ^3 -carene (5.34%), β -phellandrene (19.12%), sabinene (0.49%), 1-methyl-4-isopropyl-1, 4-cyclohexadiene (0.15%), 1,8-cineole (0.36%), 2-methyl nonane (1.65%), *o*-cymene (0.37%), n-dodecane (1.22%), verbinone (0.43%), fenchone (0.55%), cinnamaldehyde (0.28%), carvone (0.42%), anethole (0.98%), thymol (0.98%), borneol (0.73%), cumyl alcohol (0.24%), neo-isothujyl alcohol (3.45%), methyl eugenol (0.41%), longifolene (0.49%), β -bourbonene (0.73%), alloaromandrene (0.84%), β -caryophyllene (1.39%), khushilol (0.82%), *trans*- β -farnesene (8.90%), β -elemene (1.03%), β -bisabolene (1.02%), ϵ -murrulene (0.65%), 3-*m*-tolyl-2-propanol (2.04%), α -farnesene (2.00%) and 5 β H, 7 β , 10 α -selina-3, 11-diene (0.18%). The essential oil of *Selinum candollei* is mainly constituted of mono- and sesquiterpenes.

INTRODUCTION

The genus *Selinum* comprises about 16 species reported chiefly from temperate regions of the northern hemisphere. Out of these, only five species, namely *Selinum candollei*, *S. filicifolium*, *S. papyraceum*, *S. vaginatum* and *S. wallichianum* occur in Pakistan and are perennial herbs. The plants of the genus possess a remarkable medicinal value and have long been used in dropsy, gout, epilepsy, gastrointestinal ailments and fever [1]. They are considered to be expectorant, sudorific, diuretic and emmenagogue. Some of the species of this genus have been and used as nervine sedatives and in incense. Oils of the species possess hypotensive, sedative and analgesic properties [2].

Selinum candollei grows wild from 2500 to 3500 m in the Himalayas. It has been located in the North West Frontier Province and Azad Kashmir in Pakistan. Because of the specific significance of *Selinum* genus, the medicinal importance of the indigenous *Selinum candollei* is required to be closely examined. Even though the species of *Selinum* have acquired good position in the universal materia medica, yet no work has so far appeared in literature

on the chemical composition of the essential oil of these species particularly the ones growing in Pakistan. This work has, therefore, been pursued with a view to highlight the quality and chemistry of the essential oil of the Pakistani *Selinum candollei* and exploit the natural resource of the country as an item of commerce at least for its use in local materia medica.

MATERIALS AND METHODS

Mature seed of the *Selinum candollei* were collected from Kalam (Swat). The essential oil from the comminuted material was steam-distilled by using the standard procedure described in our earlier publications [3, 4]. The general methods employed for the physicochemical evaluation of the oil have already been reported [3, 4]. Because of its complex nature, the oil was studied in detail by using time and temperature-programmed GLC coupled with mass spectrometry. A Varian gas chromatograph (2100) with ionization detector was used for the resolution of the oil and identification of its various components was carried out from their mass spectra. SE-30 was used as packing material in the column and its temperature was programmed between 70–180^o at the rate of 2^o/min.

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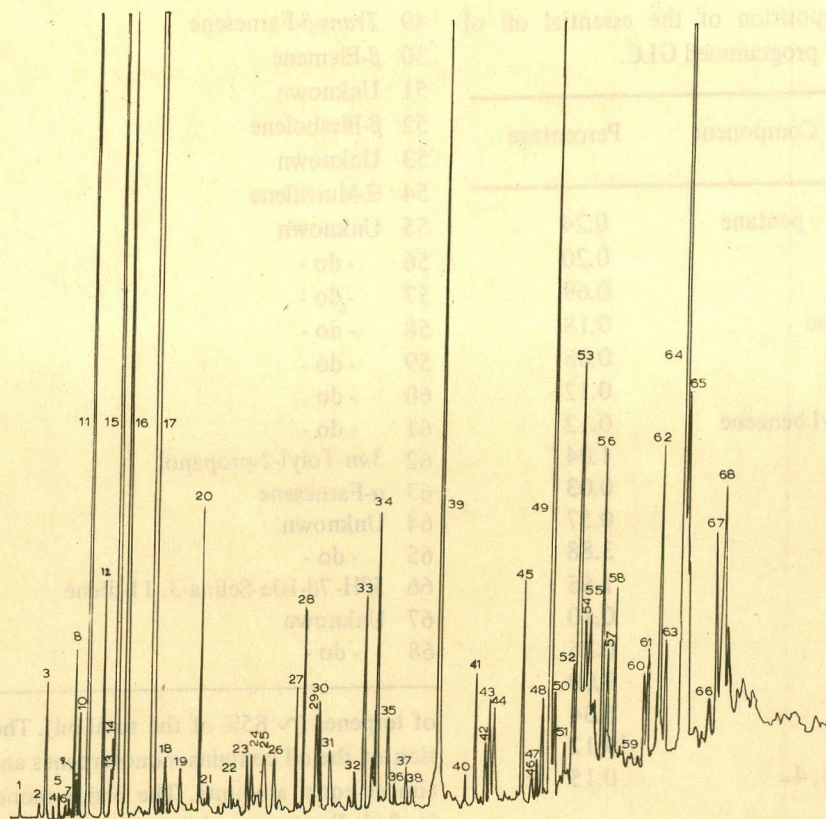


Fig. 1. Time and temperature programmed GLC of the essential oil of *Selinum candollei*.

Table 1. Percentage yield and physicochemical values of the essential oil of *Selinum candollei* seed.

Distillation time (hr)	14
Yield of the oil (%)	0.18
Specific gravity	0.9120 ²⁵
Refractive index	1.5160 ²⁵
Optical rotation	—
Acid value	8.58
Ester value	40.04

Superscripts indicate the temperature at which these parameters were determined.

RESULTS

The percentage yield, physicochemical properties and the chemical composition of the essential oil obtained from the *Selinum candollei* are reported in Tables 1–2. Resolution of the essential oil into its components by programmed GLC, is shown in Fig. 1.

DISCUSSION

The essential oil recovered from the seed of *Selinum*

was column-chromatographed on silica gel using n-hexane for the elution of hydrocarbons and progressively increasing proportions of diethyl ether (2–50%) in n-hexane for the recovery of oxygenated components. The hydrocarbon fraction of the oil which consisted of monoterpenes and sesquiterpenes was further resolved into individual components by GLC and identified against their available standard samples. The oxygenated fractions of the oil containing more than one components were rechromatographed to obtain single compounds which were identified by GLC and IR comparison with their standard samples. However, in view of a large number of the compounds, the oil was analysed by programmed GLC coupled with mass spectrometry.

Sarin and Kapoor [2] have reported the chemical composition of the essential oil distilled from the roots of *Selinum vaginatum* and identified α -pinene, β -pinene, limonene, phellandrene, fenchone and fenchyl alcohol in the oil. The seed essential oil of *Selinum mannier* was studied by Gerasimenke and Nikonov [5] for its coumarins; osthole and 6 other coumarins were separated by chromatography. However, no work has so far been reported in literature on the essential oil of *Selinum candollei*. The present work, therefore, is the first ever of its kind particularly of the Pakistani species.

Table 2. Chemical composition of the essential oil of *Selinum candollei* seed by programmed GLC.

Peak No.	Component	Percentage
1	2, 3-Dimethyl-3-ethyl pentane	0.24
2	α -Thujene	0.20
3	α -Pinene	0.69
4	Unknown monoterpene	0.18
5	Phenyl methyl ketone	0.08
6	Santene	0.12
7	1-Methyl-4-isopropenyl benzene	0.12
8	Salinene	1.04
9	2, 4-Dimethyl hexane	0.03
10	β -Pinene	0.57
11	Myrcene	3.88
12	2-Methyl nonane	1.65
13	Unknown	0.10
14	γ -Terpinene	0.25
15	<i>p</i> -Cymene	9.00
16	Δ^3 -Carene	5.34
17	β -Phellandrene	19.12
18	1-Methyl-4-isopropyl-1, 4-cyclohexadiene	0.15
19	1, 8-Cineole	0.36
20	n-Undecane	1.88
21	<i>o</i> -Cymene	0.37
22	Fenchone	0.55
23	Sabinene	0.49
24	Verbinone	0.43
25	Unknown	0.38
26	- do -	0.57
27	- do -	0.86
28	n-Dodecane	1.22
29	Cinnamaldehyde	0.28
30	Carvone	0.42
31	Unknown	0.24
32	- do -	0.20
33	Anethole	0.98
34	Thymol	0.98
35	Borneol	0.73
36	Cumyl alcohol	0.24
37	Unknown	0.18
38	- do -	0.24
39	Neo-isothujyl alcohol	3.45
40	Unknown	0.18
41	Methyl eugenol	0.41
42	Longifolene	0.49
43	β -Bourbonene	0.73
44	Alloaromadendrene	0.84
45	β -Caryophyllene	1.39
46	Unknown	0.04
47	- do -	0.43
48	Khusilol	0.82

49	<i>Trans</i> - β -Farnesene	8.90
50	β -Elemene	1.03
51	Unknown	0.47
52	β -Bisabolene	1.02
53	Unknown	1.63
54	ϵ -Murrulene	0.65
55	Unknown	0.43
56	- do -	1.80
57	- do -	0.43
58	- do -	1.23
59	- do -	0.71
60	- do -	1.22
61	- do -	0.33
62	3- <i>m</i> -Tolyl-2-propanol	2.04
63	α -Farnesene	2.00
64	Unknown	9.70
65	- do -	10.52
66	5 β H-7 β -10 α -Selina-3, 11-diene	0.18
67	Unknown	1.02
68	- do -	1.25

of terpenes ($\sim 85\%$ of the total oil). The hydrocarbon fraction of the oil contains monoterpenes and sesquiterpenes in almost equal amounts. The major monoterpene in the oil is β -phellandrene while *trans*- β -farnesene is the major sesquiterpene in the hydrocarbon fraction of the oil. The various terpenes were identified from their mass spectra.

The oxygenated fraction of the oil ($\sim 15\%$) consists of a mixture of aldehydes, ketones, alcohols, phenols and phenolic ethers. These compounds were also identified from their mass spectra. The results of mass spectra do not show any coumarin in the oil. The last column chromatographic fraction of the oil, nevertheless, when examined under UV light, indicated a small amount of coumarins.

These studies present a detailed chemical composition of the essential oil of *Selinum candollei* growing wild in Pakistan. However, bacteriostatic/bacteriocidal activities of the oil are needed to be examined. Our successful cultivation of the plant in the PCSIR Laboratories, Lahore, will then only be materialized.

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The essential oil steam-distilled from the gum resin of *Ferula assosifolia* originating from the Punjab Province in Pakistan has been studied with respect to its physicochemical characteristics and chemical composition. The oil is obtained from the gum in 30.74% yield and has been found to be composed of 8-terpenes (1+3%), sesquiterpenes (6.4%), secondary butyl propyl diastere (51.9%), undecyl sulphonic acid (15.8%), an unidentified sulphide (7.3%) and fatty material (1.0%). The essential oil possesses garlic-like flavour and it can be used in place of its gum which finds application in the preparation of some local dishes besides its unique medicinal value.

been reported in our earlier work [4, 5].
 The oil was column chromatographed using silica gel as an adsorbent. The hydrocarbon fraction of the oil was recovered with n-hexane which was further rechecked into individual components by GLC using a stainless-steel column (3 mm x 3m) nitrogen as the carrier gas and flame ionization detector. The column was operated at 110° and 135° for the resolution and identification of sesquiterpenes and sesquiterpenes respectively. The oxygenated components of the oil were eluted from the column with 2-10% diethyl ether in n-hexane. Identification of these compounds was carried out by IR comparison with their standard spectra and also by chemical methods.

RESULTS

The percentage yield, physicochemical values and chemical composition of the essential oil of *Ferula assosifolia* gum are recorded in Table I-3.

Table I. Percentage yield and physicochemical values of the essential oil of *Ferula assosifolia* gum.

Distillation time (hr)	Yield of the oil (%)	Specific gravity	Refractive index	Optical rotation	Acid value	Ester value	Ester value after acetylation
14	30.74	0.9155	1.5240	-2.11	2.32	21.49	10.94

Superscript indicates the temperature at which these parameters were determined.

INTRODUCTION

Ferula is the largest genus in the Umbelliferae family of 140 species from the Mediterranean region to the Central Asia. Most of these plants are reported to grow in the USSR and its adjacent regions. Pakistan is inhabited only 16 species of the genus *Ferula*. The plants grow wild and are perennial herbs.

Ferula assosifolia is native to Afghanistan and Iran. The plant exudes a gum which finds wide applications as a medicine [1, 2]. The gum is one of the most important species used in small quantities in most of the Indian cookery. It has since long been used in the local medicine as stimulant, carminative, antispasmodic, expectorant, laxative, diuretic, anticholeric, spasmolytic, emmenagogue and action improver. It is employed as a flavouring for sauces and other foods and for the cure of hypochondriac. The oil of the gum has been found effective against *Trichinella spiralis*, *Ascaris lumbricoides*, *Ascariasis* and *Ascariasis* [3].

The present investigation deal with the essential oil of the *Ferula assosifolia* gum to study its quality and chemical composition in view of exploring the indigenous raw material of the country.

MATERIALS AND METHODS

Ferula assosifolia gum was obtained from the Qazilla market where it is sold under the name of 'Thera Hing'. The essential oil from the gum was recovered by dry steam distillation according to the standard procedure [4]. The present methods used for the analysis of the oil have