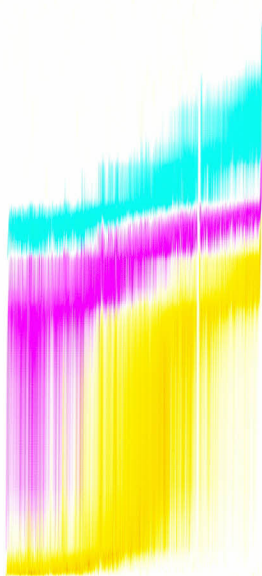


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STUDIES ON THE ESSENTIAL OILS OF THE PAKISTAN SPECIES OF THE FAMILY UMBELLIFERAE

Part III. *Cuminum cyminum* Linn. (Cumin, Safed zira) seed oil

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Abstract. The essential oil of the seed of *Cuminum cyminum* Linn cultivated in Pakistan has been studied for the first time with respect to its physicochemical constants and chemical composition. Samples of the oil as distilled from the seed of the Peshawar and Quetta regions were obtained in 3.5 and 3.0% yields and consisted of α -pinene (1.1 and 0.7%), β -pinene (14.3 and 19.7%), limonene (0.4 and 1.5%), γ -terpinene (11.5 and 16.3%) *p*-cymene (6.0 and 2.7%), cuminaldehyde (22.4 and 20.0%), 1,4-*p*-menthadien-7-al (23.6 and 24.3%), 1,3-*p*-menthadien-7-al (13.5 and 11.5%) and cuminyl alcohol (7.2 and 3.7%) respectively. The Pakistan cumin seed contains a volatile oil comparable to those recorded for seed of good commercial quality from other geographical sources.

Cuminum cyminum Linn. (cumin, safed zira) is indigenous to Egypt and its seed has been mentioned in the Ebers papyrus dating back to Biblical times. The plant has been naturalized in Pakistan and is widely cultivated in the Pakistan-India subcontinent, southern Russia and Morocco, Algeria, Syria and on the islands of Malta and Cyprus, along the southern and eastern shores of the Mediterranean.

It is reported to be cultivated in Pakistan in the Peshawar, Quetta, Sibbi and Kalat Districts and its production ranges from 500-600 tons/annum. The bulk of this quantity is brought to the markets of Peshawar and Quetta.

Cumin seed is light brown in colour and has a characteristic strong heavy and warm flavour. It is widely used as a condiment constituting one of the most important flavouring ingredients of Pakistani curries. It is also employed as an antispasmodic, astringent, stimulant, carminative, stomachic, diuretic and emmenagogue in medicine.¹

No attention has so far been paid in Pakistan to the exploitation of this valuable species as an industrial crop leading to the production and export of its essential oil. Relative merits of the local oil are also unknown. The present studies have, therefore, been carried out with a view to highlighting the quality and chemical composition of the essential oil of the cumin of Pakistan and thus determining its corresponding international commercial importance.

Experimental

Material

Mature seed of cumin cultivated in Peshawar and Quetta Districts was directly procured from these areas for the present studies.

Recovery of the Essential Oil

The essential oil was steam-distilled from the freshly ground seed according to the method described earlier.² The percentage yield of the oil and the distillation time are recorded in Table 1.

Methods

Physicochemical Constants. The instruments in the determination of various physical constants of the oil and m.p.s. of solids in these studies have already been reported. Chemical characteristics of the oil were determined according to Guenther³ and these also indicated in Table 1.

Silica Gel for Column Chromatography. Commercial silica gel was crushed to 60-80 mesh and refluxed in aqua regia for 6 hr. It was then washed neutral to litmus with tap water and finally with distilled water. The material was air-dried and activated in a furnace at 500-600° for 6 hr.

Analysis of the Essential Oil. The methods used for the analysis have already been described in our earlier publication.² A weighed quantity of the oil (about 30 g) was loaded on to a glass column (120 × 4.5 cm) packed with the gel (600 g). The hydrocarbon fraction was eluted with *n*-hexane. Elution of the oxygenated components was carried out employing successively 1, 2, 3, 5, and 20% diethyl ether in *n*-hexane as the eluent.

Individual constituents in the hydrocarbon fraction were identified and estimated by means of gas liquid chromatography (GLC) using authentic reference components. A 3 m × 3 mm copper column packed with 20% polyethylene glycol succinate (BHD) coated on Celite 60-80 mesh, was employed. The

TABLE 1. YIELD AND PHYSICOCHEMICAL CONSTANTS OF CUMIN OIL.

Constant	Essential oil from		Literature ⁴
	Peshawar	Quetta	
Time of distillation	12 hr	12 hr.	12 hr
Yield(%)	3.5	3.0	3.5
Specific gravity	0.9089 ²²	0.9071 ²²	0.9050 ²⁰ 0.9250 ²⁵
Refractive index	1.5000 ²¹	1.4980 ²¹	1.5010-1.5060
Optical rotation	+4°.47 ²¹	+4°.60 ²¹	+3 to +8°
Acid value	0.56	0.35	
Ester value	5.82	4.70	
Ester value after acetylation	28.25	23.50	
Total aldehyde by hydroxylamine method	58.50%	56.00%	45-52%

chromatograms were run at 140°, temperatures up to 180° were tried to check for the presence of sesquiterpenes.

The constituents of the hydrocarbon fraction as identified and determined by GLC and those of the oxygenated fraction as separated and estimated directly by column chromatography were recorded in Table 2.

Discussion

The yields of 3.5 and 3.0% for the essential oil from the seed of the Peshawar and Quetta regions are comparable with those recorded for similar oils of other countries. Thus the cumin seed of Malta has given a yield of 3.5-5.0%, Morocco 3.0%, East India 2.3-3.5% and Syria 2.5-4.0% of the essential oil. The physicochemical constants of the Pakistani cumin oil are also similar to those reported in literature (Table 1).⁴ The composition of the oil of some other countries has been reported mostly qualitatively by various workers; the British oil has been analysed by Hill and Umney,⁵ the Indian oil by Gupta and Patwardham,⁶ the German oil by Hans,⁷ the Bulgarian oil by Georgiev *et al.*,⁸ and the American oil by Varo and Heinz.⁹ Only the last mentioned workers have quantitatively estimated the oil components. A comparison of the Pakistani oil with these oils with respect to chemical composition is shown in Table 3.

Column chromatography employing silica gel was shown in these studies to give neat separation of hydrocarbons from the oxygenated components in the oil as established by the IR and TLC examination of the individual fractions. Nevertheless, fractions containing more than one component were further resolved using the same technique and adsorbent.

TABLE 2. COMPOSITION OF THE ESSENTIAL OILS OF CUMIN FROM PESHAWAR AND QUETTA.

Eluent	Constituents	Oil from Peshawar(%)	Oil from Quetta(%)
n-Hexane	Hydrocarbons*	(33.3)	(41.9)
	α -Pinene	1.1	0.7
	β -Pinene	14.3	19.7
	Limonene	0.4	1.5
	γ -Terpinene	11.5	16.3
	<i>p</i> -Cymene	6.0	2.7
1% Diethyl ether in n-hexane	Cuminaldehyde	22.4	20.0
2% Diethyl ether in n-hexane	1,4- <i>p</i> -Menthadien-7-al	23.6	24.3
3% Diethyl ether in n-hexane	1,3- <i>p</i> -Menthadien-7-al	13.5	11.1
20% Diethylether in n-hexane	Tarry material	Traces	Traces

*Resolved and estimated by gas liquid chromatography (GLC).

The effect of ecological conditions on the composition of the oil is well reflected by the variation in composition of the hydrocarbon fractions of the cumin oil obtained from the two different regions of Pakistan (Table 2). The oil from Peshawar contains 33.3% hydrocarbons while that from Quetta contains 41.1%. Although β -pinene and γ -terpinene are the major terpenes in both the oils, *p*-cymene is present to the extent of 6.0% in the hydrocarbon fraction of the former oil and only 2.7% that of the latter. The amount of α -pinene in the former oil is twice the quantity of α -pinene in the latter. Moreover, the Peshawar oil contains 0.4% limonene as against 1.5% in the Quetta oil.

Previously, Hill and Umney⁵ had reported the cumin oil from the U.K. to contain α -pinene and *p*-cymene as the major and dipentene and β -phellandren as the minor terpenes. The oil from India was reported to contain *p*-cymene and dipentene as the main terpenes.⁶ But the oil from Pakistan is unique in that its major terpenes are β -pinene and γ -terpinene instead of α -pinene and *p*-cymene.

Hans⁷ recovered 3-5% oil from the cumin of German origin and showed that it contained α -pinene, β -pinene, dipentene, β -phellandrene and *p*-cymene. The only difference in the hydrocarbon fractions of the German and Pakistani cumin oil lies in that β -phellandrene in the former has been replaced by γ -terpinene in the latter.

Georgiev *et al.*⁸ studied the essential oils of two varieties of cumin cultivated in Bulgaria and observed the presence of large amounts α -pinene, β -pinene, *p*-cymene and γ -terpinene; limonene which is present in the Pakistani oil was, however, missing from the Bulgarian oil.

TABLE 3. COMPARISON OF THE ESSENTIAL OIL OF THE PAKISTANI CUMIN WITH OTHER CUMIN OILS REPORTED IN LITERATURE.

Component	British ⁵	Indian ⁶	German ⁷	Bulgarian ⁸	American ^{9*}	Varo and Heinz ¹¹	Pakistan †	
							Peshawar	Quetta
α -Pinene	+	—	+	+	0.5	1.3	1.1	0.7
β -Pinene	—	+	+	+	13.0	20.1	14.3	19.7
Myrcene	—	—	—	—	0.3	0.2	—	—
α -Phellandrene	—	—	—	—	—	t	—	—
Phellandrene	+	—	+	—	+	—	—	—
<i>p</i> -Cymene	+	+	+	+	8.5	—	6.0	2.7
Limonene	+	+	+	—	—	—	0.4	1.5
β -Phellandrene	—	—	—	—	—	11.1	—	—
α -Terpinene	—	—	—	—	—	—	—	—
1, 8-cineol	—	—	—	+	0.2	—	—	—
γ -Terpinene	—	—	—	+	29.5	—	11.5	16.3
δ -Terpinene	—	—	—	—	—	18.2	—	—
β -Caryophyllene	—	—	—	—	0.8	.1	—	—
β -Farnesene	—	—	—	—	1.1	0.2	—	—
Unknown	—	—	—	—	—	0.1	—	—
β -Bisabolene	—	—	—	—	0.9	t	—	—
Unknown sesquiterpene	—	—	—	—	—	t	—	—
Sabinene hydrate	—	—	—	—	—	t	—	—
<i>trans</i> -Sabinene hydrate	—	—	—	—	—	t	—	—
<i>cis</i> -Sabinene hydrate	—	—	—	—	—	t	—	—
Unknown sesquiterpene	—	—	—	—	—	t	—	—
3, <i>p</i> -Menthen-7-al	—	—	—	—	0.7	—	—	—
Myrtenal	—	—	—	—	t	0.1	—	—
α -Terpineol	+	—	—	—	t	—	—	—
Cuminaldehyde	m	41.3	m	m	32.4	16.4	22.4	20.0
Phellendral	—	—	—	—	t	t	—	—
Perillaldehyde	+	+	+	—	—	—	—	—
1,3- <i>p</i> -Menthadiene-7-al	—	—	—	—	5.6	—	13.5	11.1
1,4- <i>p</i> -Menthadiene-7-al	—	—	—	—	—	31.5	23.6	24.3
Cuminy alcohol	+	7.2	+	—	2.8	t	72.2	3.7

+ present, but quantity not reported; —absent, m main component; t traces;

*analysed by gas liquid chromatography; † analysed by column chromatography and gas liquid chromatography.

Varo and Heinz⁹ using GLC identified α -pinene, β -pinene, myrcene, α -phellandrene, α -terpinene, limonene, β -phellandrene, *p*-cymene and γ -terpinene as the terpenic constituents and β -bisabolene, β -caryophyllene and β -farnesene as sesquiterpenes in the U.S. essential oil.

The essential oils of both the areas contain cuminaldehyde 1,4-*p*-menthadien-7-al, 1,3-*p*-menthadien-7-al and cuminy alcohol as oxygenated components. Cuminaldehyde was identified by comparing its IR spectrum with that reported in literature. On reduction with lithium aluminium hydride,¹⁰ cuminaldehyde gave cuminy alcohol, the IR spectrum of which matches with that of an authentic sample. 1,4-*p*-Menthadien-7-al and 1,3-*p*-menthadien-7-al were also identified by comparison of their IR spectrum with those reported in literature.¹¹

The British cumin oil⁵ contains cuminaldehyde as the major oxygenated constituent and α -terpineol, dihydrocuminaldehyde and cuminy alcohol in small amounts. The Indian oil⁶ contains cuminaldehyde (41.3%) and cuminy alcohol (7.2%). But the amounts of aldehydes and alcohols in the Peshawar and Quetta oils are quite high as compared with these oils which fact is indicative of the superiority of the Pakistani oil over the other oils.

According to Hans,⁷ the oil from Germany contained cuminaldehyde in larger amounts and perillaldehyde and cuminy alcohol in minor quantities. The Egyptian cumin oil as investigated by GLC was reported to contain cuminaldehyde, cuminy alcohol,

perillaldehyde, crypton and anisaldehyde.¹² Aldehydes along with 1,8-cineol are also claimed to be the constituents of the essential oils of the two varieties of the Bulgarian cumin.⁸

Varo and Heinz,⁹ however, using GLC have shown that the American oil contains 1,8-cineol, *cis*- and *trans*-sabinene hydrate, 3-*p*-menthen-7-al, myrtenal, α -terpineol, cuminaldehyde, phellendral, 1,3-*p*-menthadien-7-al, 1,4-*p*-menthadien-7-al, cuminy alcohol and many other unknown compounds.¹¹ The total aldehydes (48.0%) are again much less in this oil as compared with those (59.5%) in one of the Pakistani oils. In the present studies we were not able to isolate or detect 1,8-cineol, *cis*- and *trans*-sabinene hydrate, myrtenal, α -terpineol and phellendral by column chromatography. This is probably due to their being present in traces in the oils.

While carrying out column chromatography of the oil on activated alumina (Merck), the recovery of cuminaldehyde was observed to be only 5% as against 22% on silica gel. The rest of the aldehyde was converted by the adsorbent to a crystalline compound, m.p. 117°. It was identified as cuminic acid by IR comparison. The other two aldehydes viz. 1,4-*p*-menthadien-7-al and 1,3-*p*-menthadien-7-al could not be washed out from this adsorbent. However, comparatively larger amounts of cuminy alcohol were obtained. It is conceivable that under the conditions of the chromatography, cuminaldehyde undergoes Cannizaro's reaction to give cuminy alcohol and cuminic acid.

In the freshly distilled oil the ratio of cuminaldehyde, 1,3-*p*-menthadien-7-al and 1,3-*p*-menthadien-al, as revealed by column chromatography using silica gel was 2:2:1. But this ratio changed to 3:1:2 when the same oil has been stored for three months. It shows that disproportionation of 1,4-*p*-menthadien-7-al to cuminaldehyde and 1,3-*p*-menthadien-7-al takes place in the oil on standing for larger periods. Our observations are in accordance with the results of Varo and Heinz¹¹ who found that 1,4-*p*-menthadiene-7-al underwent disproportionations into cuminaldehyde and 3-*p*-menthen-7-al under acidic and alkaline conditions. 1,4-*p*-Menthadiene-7-al was found to isomerize into 1,3-*p*-menthadiene-7-al as to oxidize to cuminaldehyde.

In the course of our studies, 3-*p*-menthen-7-al could not be isolated by column chromatography which might be due to its very low concentration or close R_f value with one of the aldehydes present in the oil.

On the basis of the present investigations, it has been concluded that the cumin seed cultivated in Pakistan, contains a volatile oil comparable in properties to those recorded for seed of good commercial quality from other geographical sources.

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