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GC/MS Analysis of Essential Oil Composition from Selected Seed Spices

K. Ashokkumar[1] · S. Vellaikumar[2] · M. Murugan[1] · M. K. Dhanya[1] · A. Karthikeyan[3] · G. Ariharasutharsan[2] · P. Arjun[4] · P. Sivakumar[5] · S. Aiswarya[1]

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Abstract The chemical composition of essential oil (EO) isolated from dried fruits or seeds of four spices were evaluated by gas chromatography/mass spectrometry (GC/MS) analysis. EO extraction was performed by hydrodistillation method. The results revealed that yields of EO were 0.6%, 4.5%, 1.5%, and 0.8% in coriander, cumin, fennel and Indian mustard, respectively. The GC/MS analysis shown a total of 11, 14, 09 and 13 constituents in the EO isolated from coriander, cumin, fennel and Indian mustard correspondingly. Among the selected four spices, coriander EO had three major constituents linalool (54.23%), cinnamaldehyde (17.01%) and α-pinene (6.12%), while cumin EO showed five major constituents that were 1,4-p-menthadien-7-al, (31.48%), *p*-cumic aldehyde (26.65%), γ-terpinene (11.79%) and *β*-pinene (14.46%). Fennel EO had predominantly anethole (69.01%), followed by estragole (12.72%), fenchone (10.02%) and limonene (5.24%). The EO of mustard seeds registered higher concentration of 3-butenyl isothiocyanate (84.36%) and allyl-isothiocyanate (8.52%). The results presented in this paper would be useful for future investigations that could lead to the identification of the health benefits of EO from spices.

Keywords Coriander · Cumin · Fennel · Indian mustard · Essential oil

Significance Statement

Seed spices like coriander, cumin, fennel and Indian mustard commonly used for food accompaniments. Seed spices have a significant level of volatile oil content. Identification of predominant chemical constituents of the volatile oil of each seed spices is prerequisite for several applications by pharma and flavour-based industries as value addition.

Seed spices deliberated as one of the chief sources for drugs in traditional and modern medicine across the world. Coriander, cumin, fennel and Indian mustard are frequent food additions primarily used as preservatives, seasoning, colouring and flavouring agents worldwide, particularly popular in south-east Asian countries for more than two thousand years [1]. Also, spices are rich in biologically active compounds like flavonoids, carotenoids, terpenes and others [2–6]. The bioactive metabolites of these spices have various biological roles, including carminative, analgesic, aphrodisiac diuretic, stomachic, antiviral, anti-inflammatory, and antioxidant activities [7–9]. In Iranian traditional medicine, dried cumin fruit has been used for treating indigestion, flatulence, diarrhoea and epilepsy [10, 11].

The yield of essential oil (EO) from seed spices depends on environmental conditions, stage of fruit or seed maturity, season of collection and varieties. The EO of fruits/

✉ K. Ashokkumar
biotech.ashok@gmail.com

1 Cardamom Research Station, Kerala Agricultural University, Pampadumpara, Idukki, Kerala, India

2 Agricultural College and Research Institute, Tamil Nadu Agricultural University, Madurai, Tamil Nadu, India

3 Subtropical Horticulture Research Institute, Jeju National University, Jeju, Republic of Korea

4 Department of Biotechnology, PRIST Deemed University, Thanjavur, Tamil Nadu, India

5 Agricultural College and Research Institute, Tamil Nadu Agricultural University, Eachangkottai, Thanjavur, Tamil Nadu, India

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seeds of spices is extracted by hydrodistillation [3, 12]. Many bioactive compounds present in coriander, cumin, fennel and Indian mustard are predominantly contributing to their unique aroma and play a significant role as a functional food as well as pharmaceutical and nutraceutical ingredients. Earlier studies have reported nineteen coriander accessions mainly identified to possess a higher concentration of linalool (40.9–79.9%), neryl acetate (2.3–14.2%), α-pinene (1.2–7.1%) and γ-terpinene (0.1–13.6%) [7]. Furthermore, EO of Northern India grown cumin seed found to be predominant constituents of β-pinene, ρ-cymene, γ-terpinene [9].

The major constituents of fennel oil were anethole, estragole, α-pinene, and limonene, depending on the chemotype [13, 14]. The EO of Indian mustard were rich in allyl isothiocyanate (54.8%) followed by diallyl trisulphide, diallyl sulphide, and 3-butenyl isothiocyanate [15]. Based on the earlier research accounts, it is apparent that EOs of spices has been attracting immense interest by researchers across the world. Therefore, this study aimed to determine oil yield and the chemical composition of essential oils from four South Indian spices. In this study, we describe the extraction of the EO of four commonly consumed seed spices by hydrodistillation and determine the variations in their chemical composition.

The 300 g of selected four spices species (coriander, cumin, fennel, and Indian mustard) was obtained from the local supermarkets—Kerala, India, during December 2019. EO was extracted using the hydrodistillation method on a dry weight basis. A hundred grams of each spice samples were ground and transferred to a 1000 ml round bottom flask separately to which 500 ml deionized water was added. Based on the preliminary studies, the optimized run time for obtaining complete essential oil extracted by hydrodistillation method for 3 h (cumin), 3.5 h (fennel), and 4 h (coriander & mustard) and was utilized for this study. Oil yield was estimated with an average of three replications. The extracted oil was carefully collected and dried over anhydrous sodium sulphate, then stored at 4 °C in the dark until use. The yield of EO was calculated as a weight by weight basis. Essential oil (%, v/w) = volume of oil collected (ml)/weight of sample (g) × 100 [3].

The analysis of EO was carried out through gas chromatography (GC) coupled with Shimadzu mass spectrometer (MS), (GC/MS—QP2020 NX SHIMADZU, Shimadzu Corp., Tokyo, Japan). The GC equipped with a fused silica capillary column, Rxi®-5 Sil MS with a dimension of 20 m × 0.18 mm, 0.18 µm film thickness. The diluted EO injected by split mode (1:20), and the helium gas flow rate consistently maintained at 1 ml/min [3]. The oven temperature programmed at 65 °C for 3 min, and then gradually raised @ 3 °C/min to 280 °C. The injector and detector temperature set at 290 °C and 260 °C, respectively. The MS conditions were electron energy 70 eV, electron impact (EI) ion source temperature 260 °C, and transmission line temperature 280 °C. The mass scan range (m/z) was 50–650 amu, data acquired at full scan mode with solvent delay for 3 min. The constituents of EOs were identified by comparing based on linear indices relative to series of *n*-alkanes (C_8–C_{20}) at the same chromatographic conditions and by comparing retention indices with those reported in the literature [16] and stored on the MS library [NIST 10 (National Institute of Standards and Technology, Gaithersburg, MD, USA).

The extraction of EO was performed by hydrodistillation method, and an average yield of three separate analyses was 0.6%, 4.5%, 1.5%, and 0.8% (v/w) in coriander, cumin, fennel, and Indian mustard accordingly (Table 1). The oil yield of cumin (4.5%) was higher than the Sudanese type's cumin (4%) [17]. The higher level of oil content observed might be due to a change in environmental conditions as well as varieties [11, 17]. Conversely, China grown fennel has reported yield 6% oil content [18], but in our study, it is recorded only 1.5% oil content. Additionally, the present study result showed that coriander oil was twofold higher as compared to the previous report of nineteen Iranian coriander accessions (0.1–0.36%) [8]. The higher level of oil content observed could be due to change in soil type, location, season and cultivars [11].

The GC/MS analysis revealed totally of thirty-nine chemical compounds that constituted 96.15–99.81% of total EO of the four seed spices (Table 1). The EO of coriander showed eleven chemical constituents, among them two monoterpenes linalool (54.23%), and α-pinene (6.12%) and an aldehyde constituent cinnamaldehyde (17.01%) were the predominant one. These three constituents comprised 70% of the concentration of the total compounds (96.15%). Ebrahimi et al. [8] stated that linalool (40.9–79.9%) was the main constituent in all the nineteen Iranian coriander accessions. The present study revealed that EO of Indian coriander also had a considerable concentration of linalool (54.23%), which is in agreement with the earlier reports. The other major constituents of coriander EO were cinnamaldehyde and α-pinene among the 11 chemical constituents separated.

Cumin essential oil (CEO) had fourteen constituents, of them six were exhibited predominant constituents such as 1,4-p-menthadien-7-al, (31.48%), *p*-cumic aldehyde (26.65%), β-pinene (14.46%), γ-terpinene (11.79%) and 2-caren-10-al (3.81%). All the major constituents of CEO belonged to monoterpenes. Similar results reported from previous studies of cumin grown from Northern India [9]. Fennel essential oil (FEO) had nine chemical constituents. Among them, four were the major monoterpene constituents, they were anethole, estragole, fenchone, and limonene and the corresponding concentration were

Table 1 Essential oil composition in seeds of coriander, cumin, fennel and Indian mustard

Sr. No.	Constituent name	RT[a]	RI[b]	RI[c]	% Content[d]			
					Coriander	Cumin	Fennel	Mustard
1	2,2-Dimethoxybutane	4.57	685	691	2.44	–	–	–
2	3-Pentenenitrile	4.69	690	692	–	–	–	1.68
3	Allyl isothiocyanate	7.17	846	846	–	–	–	8.52
4	α-Thujene	8.33	924	930	–	0.97	–	–
5	α-Pinene	8.55	932	933	6.12	0.76	0.46	–
6	β-Pinene	9.75	943	948	–	16.46	–	–
7	3-Butenyl isothiocyanate	9.76	954	962	–	–	–	84.36
8	β-Myrcene	9.98	958	990	–	0.61	–	–
9	p-Cymene	11.00	1020	1025	–	5.24	–	–
10	Limonene	11.13	1030	1030	–	0.39	5.24	–
11	Eucalyptol	11.23	1031	1031	–	0.38	–	–
12	γ-Terpinene	11.91	1054	1059	–	11.79	–	–
13	Fenchone	12.76	1083	1086	–	–	10.02	–
14	Linalool	12.88	1086	1095	54.23	–	–	
15	Acetamide	12.99	1102	1100	–	–	–	0.32
16	Terpinen-4-ol	15.28	1174	1177	–	0.14	–	–
17	3-p-Menthen-7-al	15.60	1190	1199	–	0.97	–	–
18	Estragole	15.67	1195	1195	–	–	12.72	–
19	Cinnamaldehyde	16.87	1214	1215	17.01	–	–	–
20	Cumic aldehyde	17.80	1230	1238	–	26.65	–	–
21	Anethole	17.94	1255	1262	–	–	69.01	–
22	2-Caren-10-al	17.98	1294	1289	–	3.81	–	–
23	1,4-p-Menthadien-7-al	18.04	1297	1290	–	31.48	–	–
24	Caryophyllene	21.26	1408	1417	–	–	0.29	–
25	Cyclohexanemethanol	22.62	1510	1512	2.72	–	–	–
26	Furfuryl octanoate	28.50	1560	1566	3.53	–	–	–
27	Coumarin	29.26	1987	1987	1.93	–	–	0.38
28	Octadecenoic acid	29.32	2091	2101	2.90	–	–	0.88
29	Adipic acid	29.42	2094	2137	–	–	–	0.50
30	Methyl 12-thia-octadecanoate	29.50	2128	2133	3.56	–	–	–
31	Hexadecanoic acid	29.54	2130	2143	–	–	–	0.74
32	Methyl 10-oxo-8-decenoate	29.61	2190	2190	–	–	0.49	–
33	Butyl 9-octadecenoate	29.68	2383	2382	–	0.16	–	0.21
34	Aminoacetamide	29.70	2524	2524	–	–	–	0.31
35	Docosanoic acid	35.19	2564	2567	–	–	0.18	–
36	Diethylmalonic acid	35.48	2571	2571	–	–	–	0.49
37	Oxiranedodecanoic acid	35.60	2617	2619	–	–	–	0.56
38	Heptadecanoic acid	35.80	3027	3036	–	–	0.28	–
39	Fumaric acid	36.40	3182	3182	1.71	–	–	0.14
	Number of constituents	–	–	–	11	14	09	13
	Total essential oil (%)	–	–	–	0.6	4.5	1.5	0.8
	Total compounds (%)	–	–	–	96.15	99.81	98.71	99.09

[a]RT = Retention time; [b]RI = Retention index (experimental) on Rxi®-5 Sil MS column; [c]RI = Retention index in literature [20]; [d]Average quantitative composition by peak area normalization; response factor for

each component was considered equal to 1. For each oil three replicates for each sample; (-), not detected; Monoterpenes: Sr. Nos. 4–6, 8–14, 16–18, 21–23; Aldehydes: 19 & 20; Esters: 26–33; Acids: 35–39; Sesquiterpenes: 24; alcohols: 25; Amides: 15, 34; others: 1–3, 7

69.01%, 12.72%, 10.02%, and 5.24%. The present study observed that the predominant constituent of FEO anethole (69.01%) was twofold greater than that found in the Tajikistan grown fennel (36.80%) [18].

Thirteen chemical constituents identified in the EO of mustard; of them, 3-butenyl isothiocyanate (84.36%) and allyl-isothiocyanate (8.52%) were the predominant once and they comprised – 92% of the total concentration. These two key constituents were also major constituents of china grown *Brassica juncea* oil [19]. Additionally, the present study gave wide variation in the chemical composition of EOs constituents compared to earlier reports. The presence of biologically active molecules of major constituents in the EO of four spices serves as a new potential source for monoterpenes and aldehydes, which can be used in food, aroma, and pharmaceutical applications. Future studies need to be done on the bioavailability and pharmacokinetics of these spices to look for the chemical constituents responsible for its activities and potency.

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