AKADÉMIAI KIADÓ

Acta Chromatographica

34 (2022) 2, 197–202

DOI:
10.1556/1326.2021.00909

ORIGINAL RESEARCH PAPER

Phytochemical profiling of spiny coriander (*Eryngium foetidum* L.) – A potential perennial spicing-culinary herb of eastern India

GOBINDA CHANDRA ACHARYA[1*], NARESH PONNAM[1], MEENU KUMARI[1], TAPAS KUMAR ROY[2], KODTHALU SEETHARAMAIAH SHIVASHANKARA[2] and MANAS RANJAN SAHOO[1**]

[1] Central Horticultural Experiment Station, ICAR-Indian Institute of Horticultural Research Regional Station, Bhubaneswar, 751019, India

[2] Division of Plant Physiology and Biochemistry, ICAR-Indian Institute of Horticultural Research, Bengaluru, 560089, India

Received: March 31, 2021 • Accepted: May 8, 2021
Published online: June 8, 2021

ABSTRACT

Spiny coriander (*Eryngium foetidum* L.) is a perennial medicinal herb grown in the tropical regions worldwide. In India, it is used as a potential spice for garnishing and flavoring the dishes and treating several ailments. *Eryngium* spp. found in coastal Odisha, India has a strong aroma similar to the seasonal *Coriandrum*. The volatile flavor constituents of the unique plants were analyzed through headspace solid-phase microextraction (HS-SPME) using capillary gas chromatography (GC) and gas chromatography-tandem mass spectrometry (GC–MS/MS). The volatile compounds exhibited high chemodiversity, with 10-undecenal as the major component in leaves (44.98%) and branches (57.43%). Fourier-transform infrared (FTIR) spectroscopy identified eight major peaks grouped into six main regions. Chemo profiles of these two corianders were overlapped and showed similar area differences in the spectral peak. The lesser-known perennial *Eryngium* with high chemodiversity would be a better alternative to the seasonal coriander for aromatic, pharmaceutical, and industrial uses.

KEYWORDS

FTIR, GC-MS analysis, volatiles, spiny coriander, aromatic and pharmaceutical industries

INTRODUCTION

Eryngium foetidum L. belongs to the family Apiaceae is a neglected perennial herb commonly known as spiny coriander. It is extensively grown in the tropics of the world for its medicinal values and unique pungency. *E. foetidum* is indigenous to tropical America and Caribbean islands and was later introduced to Southeast Asian countries by the Chinese in the late 1800s. This perennial herb is grown abundantly in the poor and marginal soils of India's eastern and north-eastern parts [1]. Leaves and branches of the plant are rationally used to garnish and flavoring foods as a substitute for coriander due to similar aroma and fragrance [2]. *E. foetidum* also has several pharmaceutical applications such as anticlastogenic [3], anti-inflammatory [4], anthelmintic and anticarcinogenic properties [1]. Leaves of this underutilized herb contain the essential oil eryngial (0.29%, trans-2-dodecenal) have many industrial applications [5]. The *Eryngium* extracts, rich in eryngial have been used effectively in treating parasites [6, 7], arthritis, and skin diseases [1]. It has also been used as a major ingredient for developing skin-whitening agents [8].

E. foetidum has a broad scope from the industrial perspective because of its wide adaptability, perennial nature, and sturdy stature. With increasing health concerns, the

*Corresponding author.
E-mail: gobinda.acharya@icar.gov.in

**Corresponding author. Tel.: +91 674 2471867; fax: +91 674 2471712.
E-mail: manas.sahoo@icar.gov.in

demands of *Eryngium* leaves are increasing for medicinal and industrial uses. Due to bioactive compounds, several *Eryngium* spp. have been used to treat human physiological disorders [9, 10, 11]. Although reports on pharmaceutical applications of *E. foetidum* are available, phytochemical investigation of leaves and the branches of *E. foetidum*, in particular, are scanty [12, 13, 14]. Hence, the present study focused on phytochemical profiling of the leaves and branches of *E. foetidum*, collected from east-coast India, through GC and GC–MS/MS to explore its industrial potential.

EXPERIMENTAL

Plant materials

E. foetidum L. plants (Biological reference material number-IC 0629514) collected from Delang, Odisha, India, and *Coriandrum sativum* L. collected from the local market were maintained in the greenhouse at Central Horticultural Experiment Station (CHES), Bhubaneswar, India. Fresh *Eryngium* leaves and branches were assessed for various phytochemical compositions and compared with coriander leaf samples (*C. sativum* L.) using FTIR spectroscopy.

FTIR analysis

The absorption spectra were measured through FTIR spectroscopy instrument Spectrum Two (Perkin Elmer Spectrum Version 10.4.3, Waltham, Massachusetts, USA) with a detector LiTa03, and experimental results were visualized using PC-based software. Intact *Eryngium* and *Coriandrum* leaf and branch samples were used for analysis, and a thin film was used for applying optimum pressure. Absorbance was recorded in the wave range from 450 to 4000 cm^{-1}, and functional groups in the samples were identified by comparing the spectral data with reference peaks.

SPME Extraction of volatiles

The extraction and analysis of headspace volatile compounds from leaves were studied using SPME fibers for direct sampling to avoid interference from nonvolatile matrices [15, 16, 17]. An SPME holder and three commercially available SPME fibers containing different adsorbents were obtained from Supelco Inc. (Bellefonte, PA, USA). Highly crossed linked (50/30 µm) DVB/CAR/PDMS was optimized as the most suitable fiber and was activated at 250°C for 3 h in the injector port, followed by the extraction in the headspace.

Headspace volatile compounds from *Eryngium* leaves and branches were extracted following standard procedure [15, 17]. Six leaves were ground and transferred into two separate 100-mL conical flasks having screwcaps with a silicon rubber septum. After closing the cap, the leaves were allowed to reach room temperature (25±1°C) to get equilibrated with headspace. The volatile compounds were absorbed by inserting the pre-conditioned SPME fiber into the headspace of the vial for 3 h.

Capillary gas chromatography and mass spectrometry (GC/MS)

Gas Chromatography (GC): For GC, a Varian CP-3800 gas chromatograph with a Varian factor FOURVF-5MS silica capillary column (30 m and 0.25-µm film thickness) and an FID detector was used. The SPME fiber was introduced in the injector port for 10 min for desorption. All injections were made in the split mode (1:5), and helium at 1 mL min^{-1} was used as the carrier gas. Injector and detector temperatures were set at 260°C and 270°C, respectively. For the column, temperature programs were maintained as follows: 50°C for 5 min, increased to 170°C at 4°C min^{-1}, then hold for 2 min, then increased to 250°C at 5°C min^{-1}, maintained a constant temperature for 7 min, and total run time was 60 min.

Gas chromatography-mass spectrometry: For resolving the components, a Varian-4000 ion-trap mass spectra detector coupled with a Varian-3800 gas chromatograph and fused-silica capillary column VF-5MS (factor Four, Varian, USA, 30 m × 0.25 mm id 0.25-mm film thickness) was used. Helium gas with a flow rate of 1 mL min^{-1} was used as a carrier. Temperatures of 200°C, 240°C, and 210°C were maintained for the ion trap, transfer line, and ion source, respectively. The mass spectrometer was operated in the external electron ionization mode of 70 eV, with a total mass scan range of 50–450 amu. Temperature programs for the column were the same as described for GC–FID.

The individual compounds resolved were quantified as the relative percent area and identified by comparing the retention index [18]. The spectral identification was made using the spectral libraries, Wiley-2005 and NIST-2007.

RESULTS AND DISCUSSION

FTIR spectroscopy

FTIR is known for its broad spectrum of uses ranging from chemical mapping/metabolite profiling to genotype identification [19]. In the present study, FTIR spectroscopy was used to identify functional groups between 450 and 4000 cm^{-1}, and functional groups were resolved based on their peaks. Individual peaks were identified and characterized according to Coates (2006) [20]. Eight major peaks were obtained from both coriander and wild spiny coriander samples. These eight peaks are described in six main regions, namely, hydroxyl region (O-H stretching) at 3337–3341 cm^{-1}, lipid region at 2918–2950 cm^{-1}, one peak of CH_2 asymmetric (2918 cm^{-1}) and CH_2 symmetric (2950 cm^{-1}), ester and olefinic region (C=O carbonyl stretch, C-H aromatic stretch, and vinyl C-H) at 1605–1420 cm^{-1}, aromatic amino groups (aromatic primary C-N stretch) at 1244 cm^{-1}, primary and secondary alcohol stretch at 1000–1100 cm^{-1}, and fingerprint region with several overlapping peaks at 1000–500 cm^{-1}. The broad and strong peak centered at 3339 cm^{-1} represents alcohol and hydroxyl group frequencies, which results from the extensive intermolecular and intramolecular hydrogen bonding of water and biomolecules

having –NH and –OH groups in a chemical structure [21, 22]. The spectra results indicated the presence of a narrow and sharp peak for $-CH_2$ asymmetric and symmetric stretching vibrations at 2918 and 2950 cm^{-1}, respectively. The integrated absorption (indicated in parentheses) by spiny coriander and coriander showed substantial long-chain fatty acids to spectral features in the lipid region. FTIR spectra for the carbonyl group are characteristic in the wave range 1605–1630 cm^{-1} located at 1618 cm^{-1} assigned for C=O ester and C-H aromatic, which might be due to the decenal group ($C_{12}H_{22}O$) and trimethylbenzaldehyde. The broad peak of the alkene group at 1419 cm^{-1} indicates unsaturated hydrocarbons that contribute to approximately 22% of total isolated compounds (Table 1). The small peak at 1244 cm^{-1} is considered for aromatic C-N stretch as 1250–1360 cm^{-1} is characteristically identified for primary, secondary, and tertiary aromatic amino groups [20]. These characteristic absorbance spectra present in the IR region of *Coriandrum* and *Eryngium* are considered spectral characteristics of flavoring compounds. The wave range 1014–1105 cm^{-1} corresponded to the alcohol stretch spectral features with primary and secondary bonds, respectively. The overlapping peaks in the wave range 450–1000 cm^{-1} are considered the fingerprint region. The *Eryngium* and *Coriandrum* profiles were overlapped, and similar patterns were observed for both the coriander with area differences in the spectral peak. Based on the above interpretation, referral spectra (Fig. 1) depicting all identified regions for coriander or coriander group plants like Culantro and Vietnamese coriander. In our study, eight major peaks were obtained from both coriander and wild spiny coriander samples (Fig. 1). The FTIR spectroscopy preliminarily showed the comparable potential of perennial spiny coriander with the perishable seasonal coriander. The result suggests further partitioning of volatile and non-volatile compounds in this lesser-known spiny coriander for exploration as a commercial food crop for industrial importance.

Table 1. FTIR peak and integrated peak area, comparison of *Eryngium foetidum* and *Coriandrum sativum*

Peak no.	Wavelength range	Peak centre	*E. foetidum*		*C. sativum*	Functional group	Reference
			leaf	branch			
1.	3337–3341	3339	3339 (65.04)	3341 (66.20)	3338 (74.94)	Intermolecular bonded alcohol O-H stretching	Silverstein et al., 2005 [19]
2.	2918	2918	2918 (2.59)	2918 (2.51)	2918 (1.7)	CH_2 asymmetric	Silverstein et al., 2005 [19]
3.	2850	2850	2850 (3.66)	2851 (2.77)	2850 (2.33)	CH_2 symmetric	Silverstein et al., 2005 [19]
4.	1605–1630	1630	1618 (9.88)	1632 (10.68)	1632 (8.22)	C=O ester, C-H aromatic	Silverstein et al., 2005 [19]
5.	1415–1420	1419	1419 (1.53)	1418 (1.82)	NA	Vinyl C-H in plane bend (olefenic/alkene group)	Silverstein et al., 2005 [19]
6.	1244	1244	NA	NA	1244 (0.79)	Aromatic primary amine, C-N stretch	Silverstein et al., 2005 [19]
7.	1100–1105	1102	1100 (0.88)	1098 (0.08)	1104 (0.62)	Secondary alcohol, C-O stretch	Marechal and Chanzy, 2000 [31]
8.	1014–1019	1017	1015 (1.81)	1030 (0.08)	1019 (0.44)	Primary alcohol, C-O stretch	Marechal and Chanzy, 2000 [31]
9.	450–1000		Overlapping peaks			Fingerprint region	Silverstein et al., 2005 [19]

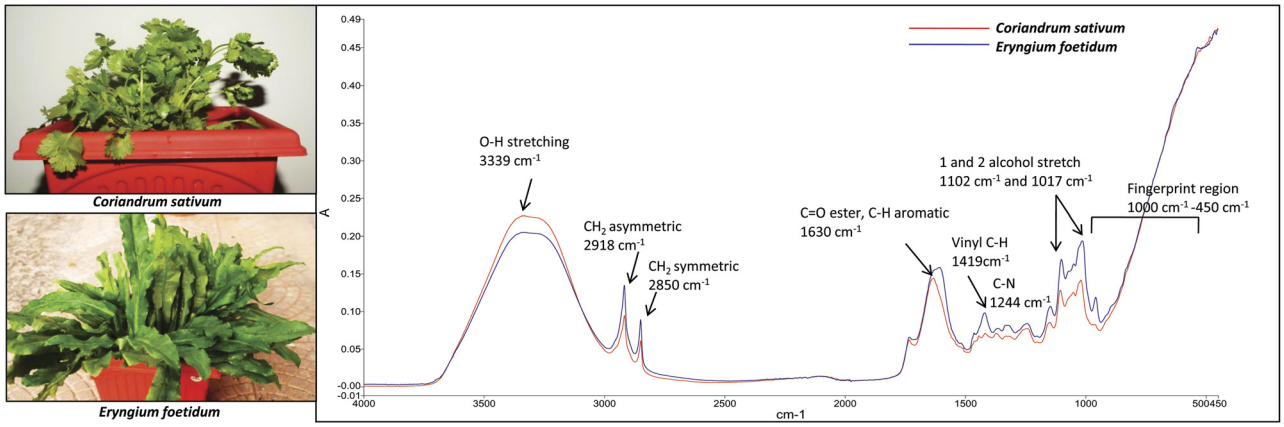

Fig. 1. Spectral characteristics of *Eryngium foetidum* L. and *Coriandrum sativum* L. through Fourier-transform infrared (FTIR) spectroscopy

GC-MS analysis

GC and GC–MS identified 77 compounds in the leaf, and 79 compounds in the branch (Table 2) of *E. foetidum* L. (IC0629514) collected from Odisha, India. In leaf volatile compounds, the major portion was contributed by aldehydes and ketones (64.63%), followed by 22.07% hydrocarbons, 7.61% alcohols, and 6% acids and oxygenated compounds. Among the aldehydes and ketones with high economic importance in aromatic industries, 10-undecenal is the dominant constituent (44.98%). (Z)-7-tetradecenal (4.35%) and (Z)-9-tetradecenal (5.42%) were other compounds of the decenal group. The isomers of trimethylbenzaldehyde [2,4,6-trimethylbenzaldehyde (7.81%) and 2,4,5-trimethylbenzaldehyde (0.41%)] are isolated moderately. These isomers were reportedly contributing to fragrance in *Eryngium* accessions of Cuba (2,4,5-trimethylbenzaldehyde; 20.53%) [23], Portugal (2,3,6-trimethylbenzaldehyde; 23.7%) [24], and Port Blair (trimethylbenzaldehyde; 16.5%) [25].

The cis-2-methyl-2-butenoic acid (0.03%) and caryophyllene oxide (0.25%) are major constituents among acids and oxygenated compounds, respectively. Beta-caryophyllene (7.09%), trans-beta-farnesene (3.56%), valencene (2.39%), germacrene D (1.51%), beta-gurjunene (1.45%), beta-bisabolene (1.39%), (Z,E)-alpha-farnesene (1.22%), and isoledene (1.06%) were important compounds among hydrocarbons. (Z)6-(Z)9-pentadecadiene-1-ol (2.31%), 1-decanol (1.39%), (Z)-7-tetradecenol (1.35%), and carotol (1.02%) were major compounds of alcohols.

The branches of *E. foetidum* L. contained the same compounds as leaves. Four primary aliphatic aldehydes [10-undecenal (57.43%), (Z)-9-tetradecenal (6.67%), (Z)-7-tetradecenal (5.34%), and 2,4,6-trimethylbenzaldehyde (4.14%)] contributed the highest (73.58%), which is 10% more than its leaf aldehydes. Only three hydrocarbons namely, beta-caryophyllene (4.9%), beta-gurjunene (3.61%), and trans-beta-farnesene (1.55%), and three alcoholic compounds, 1-decanol (1.24%), (Z)-7-tetradecenol (1.88%), and (Z)6-(Z)9-pentadecadiene-1-ol (1.26%), contributed above 1%. These hydrocarbons and alcoholic compounds also contributed more than 1% of their leaf essential oils. Almost the same proportion of acids and oxygenated compounds was present in the essential oil from the branches and leaves. The leaves with the branch portion of this sturdy herb may be used for isolation of the flavoring compounds.

The chemical constituents reportedly varied among the *Eryngium* spp. collected from different geographical locations. However, (E)-2-dodecanal, a major aliphatic aldehyde compound found common in *Eryngium* leaves of various geographical origins such as the Vietnam origin (45.5%) [26], Peang Hill (Malaysia) origin (59.7%) [27], Bangladesh origin (37.5%) [12], Northeastern hill region of India (38.9%) [1], Southern Vietnam origin (57.8%–67.1%) [28], Peruvian origin (61.6%–62.2%) [29], and Nadugani Indian accessions (2.8%) [25]. In the Eastern Ghats genotypes of India, (E)-2-dodecanal was found in a minor quantity in leaf (0.021%) and branch (0.032%) [25]. Wide variation in the (E)-2-dodecanal content probably due to the adverse

Table 2. Percentage composition of different compounds in leaves and branches of *Eryngium foetidum* L. analyzed through GC and GC-MS

Compounds Identified	K.I Cal.	% composition	
		Leaf	Branch
Hydrocarbons			
Toluene	762	0.008	0.01
α-Thujene	923	0.008	0.005
α-Pinene	932	0.225	0.099
Sabinene	971	0.034	0.018
β-Pinene	978	0.334	0.259
trans-4-Decene	995	0.010	0.116
Decane	1000	0.179	0.086
δ- 3-carene	1009	0.003	0.004
1,2,3-Trimethylbenzene	1017	0.037	0.123
α-Terpinene	1019	0.003	0.002
Limonene	1033	0.161	0.126
cis-Ocimene	1026	0.016	0.008
β-Ocimene	1041	0.014	0.001
Benzene, 1-methyl-4-(2-propenyl)-	1048	0.008	0.008
γ-Terpinene	1062	0.307	0.192
Terpinolene	1085	0.003	0.002
3-Butyl-4-vinyl-1-cyclopentene	1092	0.007	0.003
4-Decene, 4-methyl-, (E)-	1100	0.003	0.009
2,6-Dimethyl-1,3,5,7-octatetraene, E,E-	1115	0.004	0.003
1-Dodecyne	1212	0.019	0.024
P-Cymene		0.100	0.117
Azulene	1305	0.001	0.007
(+)-Cyclosativene	1317	0.180	0.055
(-)-Isosativene	1339	0.089	0.043
(-)-Isoledene	1381	1.067	0.398
β-Gurjunene	1405	1.454	3.615
Thujopsene	1421	0.126	0.128
β-Caryophyllene	1427	7.091	4.903
α-Bergamotene	1432	0.350	0.152
Germacrene D	1464	1.517	0.735
(+)-Valencene	1474	2.396	0.152
(Z,E)-α-Farnesene	1478	1.229	0.464
γ-Muurolene	1486	0.506	0.198
trans-β-Farnesene	1506	3.563	1.552
β-Bisabolene	1512	1.390	0.000
(-)-β-Cadinene	1518	0.329	0.000
Alcohols			
Cis-3-Hexen-1-ol	852	0.135	0.098
1-Hexanol	864	0.017	0.010
5-Octen-1-ol, (Z)-	1067	0.038	0.047
3-Nonen-1-ol, (E)-	1167	0.022	0.030
Methyl Chavicol	1192	0.112	0.118
E-2-Decenol	1261	0.021	0.032
1-Decanol	1268	1.396	1.249
2,4-Undecadien-1-ol	1379	0.203	0.216
2,4-Undecadienol	1385	0.000	0.051
8,10-Dodecadien-1-ol, (E,E)-	1473	0.033	0.000
6-Dodecenol	1485	0.340	0.318
(2E,4E)-2,4-Decadien-1-ol	1491	0.000	0.029
Nerolidol	1564	0.228	0.090
5,7undecadienol	1583	0.286	0.379
(+)-Carotol	1591	1.026	0.268
(Z)-7-Tetradecenol	1663	1.350	1.880
(Z)-9-Tetradecen-1-ol	1671	0.152	0.548

(continued)

Table 2. Continued

Compounds Identified	K.I Cal.	% composition	
		Leaf	Branch
(Z)6-(Z)9-Pentadecadiene-1-ol	1782	2.315	1.258
Aldehydes and Keto			
1-Hexanal	788	0.006	0.005
(E)-2-Hexenal	860	0.191	0.103
(Z)-6-Nonenal	1102	0.121	0.650
2,4-Dimethylbenzaldehyde	1180	0.042	0.094
(4E)-4-Undecenal	1191	0.470	0.734
Safranal	1198	0.104	0.092
β-Cyclocitral	1210	0.012	0.003
(Z)-2-Decenal	1253	0.354	0.128
(2E,4E)-2,4-Decadienal	1288	0.055	0.033
10-Undecenal	1293	44.981	57.438
2,4,5-Trimethylbenzaldehyde	1301	0.414	0.299
Benzaldehyde, 2,4,6-trimethyl-	1316	0.000	0.014
2,4,6-Trimethylbenzaldehyde	1324	7.811	4.142
7- dodecen-1 –al	1395	0.017	0.064
5,9,9-Trimethylspiro[3.6]deca-5,7-dien-1-one	1473	0.000	0.005
(E,E)-2,4-Dodecadien-1-al	1491	0.000	0.224
Z-7-Tetradecenal	1585	4.359	5.347
(Z)-9-Tetradecenal	1606	5.421	6.678
13-Tetradecenal	1610	0.008	0.007
(Z)-9-Hexadecenal	1792	0.157	0.235
(13Z)-13-Octadecenal	2007	0.172	0.018
Acids			
cis-2-Methyl-2-butenoic acid	860	0.033	0.031
Oxygenated			
Pyrazine, 2-methoxy-3-(1-methylpropyl)-	1175	0.004	0.004
2-Isopropyl-1-methoxy-4-methylbenzene	1231	0.019	0.002
2-Pentyl furan		0.060	0.080
2-Octylfuran	1290	0.088	0.060
2-Chloro-5-methoxy-1,3-dimethylbenzene	1292	0.004	0.014
Caryophyllene oxide	1581	0.254	0.310

climatic factors and herbage. The well-known spicy herb coriander leaves are the primary source of decanal group volatile compounds such as (E)-2-decanal, (E)-2-dodecanal, (E)-2-undecanal, and (E)-2-tetradecanal of coriander leaves and herb [19, 30]. The phytochemical study of spiny coriander shows that the 10-undecenal group (C_{10}) is the major component that attributes to aromatics, indicating the herb can be used as a substitute for *Coriandrum* in pharmaceutical industries.

CONCLUSIONS

Eryngium collected from Odisha, India, exhibited high chemodiversity with 10-undecenal as the major component in leaves (44.98%) and branches (57.43%) followed by 2,4,6 trimethylbenzaldehyde (7.81% in leaves and 4.14% in the branches), (Z)-9-tetradecenal (5.42% in leaves and 6.67% in the branches), and (Z)-7-tetradecenal (4.35% in leaves and 5.34% in the branches). Chemo profiles of these two corianders, *Eryngium* and *Coriandrum*, were overlapped and showed similar area differences in the spectral peak. Perennial sturdy *Eryngium*, well suited to poor and marginal soils, can be promoted for large-scale production of aromatic compounds and flavonoids for industrial use alternate to perishable seasonal *Coriandrum*.

Disclosure statement: The authors declare that there is no conflict of interest.

Author contribution statement: GCA: Conceptualization, Validation, Writing -original draft, Supervision. NP: Methodology, Investigation, Formal analysis, Writing -original draft. MK: Methodology, Investigation, Formal analysis, Writing -original draft. TKR: Investigation, Formal analysis. KSS: Formal analysis. MRS: Validation, Writing -review and editing.

ACKNOWLEDGEMENTS

The authors thank the Director of the Indian Institute of Horticultural Research, Bengaluru, India, for providing facilities and Central Instrumentation Facilities (CIF), Odisha University of Agriculture and Technology, India for FTIR analysis of the samples.

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