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

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**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,
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 crosslinked (50/30 m) 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\(_3\) 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 –CH₂ 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 (C₁₂H₂₂O) 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 corianders 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.

| Peak no. | Wavelength range | Peak centre | E. foetidum | C. sativum | Functional group | Reference |
|---------|------------------|-------------|-------------|------------|-----------------|-----------|
| 1       | 3337–3341        | 3339        | 3339        | 3338       | Intermolecular bonded alcohol | Silverstein et al., 2005 [19] |
|         | (65.04)          | (66.20)     | (74.94)     | (66.20)    |                  |           |
| 2       | 2918             | 2918        | 2918        | 2918       | CH₂ asymmetric   | Silverstein et al., 2005 [19] |
|         | (2.59)           | (2.51)      | (1.7)       | (2.51)     |                  |           |
| 3       | 2850             | 2850        | 2850        | 2850       | CH₂ symmetric    | Silverstein et al., 2005 [19] |
|         | (3.66)           | (2.77)      | (2.33)      | (2.77)     |                  |           |
| 4       | 1605–1630        | 1618        | 1618        | 1632       | C=O ester, C-H aromatic | Silverstein et al., 2005 [19] |
|         | (9.88)           | (10.68)     | (8.22)      | (10.68)    |                  |           |
| 5       | 1415–1420        | 1419        | 1419        | NA         | Vinyl C-H in plane bend (olefinic/alkene group) | Silverstein et al., 2005 [19] |
|         | (1.53)           | (1.82)      | NA          | (1.82)     |                  |           |
| 6       | 1244             | 1244        | 1244        | NA         | Aromatic primary amine, C-N stretch | Silverstein et al., 2005 [19] |
|         | (0.79)           | (0.79)      | NA          | (0.79)     |                  |           |
| 7       | 1100–1105        | 1100        | 1100        | 1104       | Secondary alcohol, C-O stretch | Marechal and Chanzy, 2000 [31] |
|         | (0.88)           | (0.88)      | (0.62)      | (0.88)     |                  |           |
| 8       | 1014–1019        | 1017        | 1017        | 1019       | Primary alcohol, C-O stretch | Marechal and Chanzy, 2000 [31] |
|         | (1.81)           | (0.08)      | (0.44)      | (0.08)     |                  |           |
| 9       | 450–1000         | Overlapping peaks | Overlapping peaks | 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-butenic acid (0.03%) and carophyllene oxide (0.25%) are major constituents among acids and oxygenated compounds, respectively. Beta-carophyllene (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 isoeledene (1.06%) were important compounds among hydrocarbons. (Z)-6-(Z)-9-pentadecadiene-1-ol (2.31%), 1-decen-1-ol (1.06%) were important compounds among hydrocarbons. (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

| Compounds Identified                        | K.I % | Cal. % | Leaf % | Branch % |
|--------------------------------------------|-------|--------|--------|----------|
| Hydrocarbons                                |       |        |        |          |
| Toluene                                     | 762   | 0.008  | 0.01   |
| alpha-Thuene                                 | 923   | 0.008  | 0.005 |
| alpha-Pinene                                 | 932   | 0.225  | 0.099 |
| Sabinene                                     | 971   | 0.034  | 0.18  |
| beta-Pinene                                  | 978   | 0.334  | 0.259 |
| trans-4-Decene                               | 995   | 0.010  | 0.116 |
| Decane                                      | 1000  | 0.179  | 0.086 |
| beta-3-carene                                | 1009  | 0.003  | 0.004 |
| 1,2,3-Trimethylbenzene                       | 117   | 0.037  | 0.123 |
| alpha-Terpine                                | 1019  | 0.003  | 0.002 |
| Limonene                                     | 1033  | 0.161  | 0.126 |
| cis-Ocimene                                  | 1026  | 0.016  | 0.008 |
| beta-Ocimene                                 | 1041  | 0.014  | 0.001 |
| Benzene, 1-methyl-4-(2-propenyl)-            | 1048  | 0.008  | 0.008 |
| gamma-Terpine                                | 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-1-(E)                     | 1100  | 0.003  | 0.009 |
| 2,6-Dimethyl-1,3,5,7-octatetraene, E,E-      | 1115  | 0.004  | 0.003 |
| 1-Dodeceny                                   | 1212  | 0.019  | 0.024 |
| P-Cymene                                     | 1243  | 0.250  | 0.152 |
| Beta-gurjunene                               | 1405  | 1.454  | 3.615 |
| Thujopsene                                   | 1421  | 0.126  | 0.128 |
| alpha-Bergamotene                            | 1427  | 7.091  | 4.903 |
| Germacrene D                                 | 1464  | 1.517  | 0.735 |
| alpha-Valencene                              | 1474  | 2.396  | 0.152 |
| (Z,E)-alpha-Farnesene                        | 1478  | 1.229  | 0.464 |
| gamma-Murolene                               | 1486  | 0.506  | 0.198 |
| trans-beta-Farnesene                         | 1506  | 3.563  | 1.552 |
| beta-Bisabolene                              | 1512  | 1.390  | 0.000 |
| (1,2)-Cadine                                 | 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-Undecadien-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 |
| 5,7-Undecadienol                             | 1583  | 0.286  | 0.379 |
| (1,2)-Carotol                                | 1591  | 1.026  | 0.268 |
| (Z)-7-Tetradecon-1-ol                        | 1663  | 1.350  | 1.880 |
| (Z)-9-Tetradecon-1-ol                        | 1671  | 0.152  | 0.548 |

(continued)
Table 2. Continued

| Compounds Identified                              | KI Cal. | % composition  |
|---------------------------------------------------|---------|----------------|
| (Z6)-(Z)9-Pentadecadiene-1-ol Aldehydes and Keto  | 1782    | 2.315          |
| 1-Hexanal                                         | 788     | 0.006          |
| (E)-2-Hexenal                                     | 860     | 0.191          |
| (Z)-6-Nonenal                                     | 1102    | 0.121          |
| 2,4-Dimethylbenzaldehyde                          | 1180    | 0.042          |
| (4E)-4-Undecenal                                  | 1191    | 0.470          |
| Safranal                                          | 1198    | 0.104          |
| β-Cyclocitral                                     | 1210    | 0.012          |
| (Z)-2-Decenal                                     | 1253    | 0.354          |
| (2E,4E)-2,4-Decadienal                            | 1288    | 0.055          |
| 10-Undecenal                                      | 1293    | 44.981         |
| 2,4,5-Trimethylbenzaldehyde                       | 1301    | 0.414          |
| Benzaldehyde, 2,4,6-trimethyl-                     | 1316    | 0.000          |
| 2,4,6-Trimethylbenzaldehyde                       | 1324    | 7.811          |
| 7-dodecen-1-one                                   | 1395    | 0.017          |
| 5,9,9-Trimethylspiro[3.6]deca-5,7-dien-1-one      | 1473    | 0.000          |
| (E,E)-2-Dodecadienal                              | 1491    | 0.000          |
| Z-7-Tetradecenal                                  | 1585    | 4.349          |
| (Z)-9-Tetradecenal                                | 1606    | 5.421          |
| 13-Tetradecenal                                   | 1610    | 0.008          |
| (Z)-9-Hexadecanal                                 | 1792    | 0.157          |
| (13Z)-13-Octadecanal                              | 2007    | 0.172          |
| Acids                                             | 860     | 0.033          |
| cis-2-Methyl-2-butenolic acid Oxygenated           | 1175    | 0.004          |
| Pyrazine, 2-methoxy-3-(1-methylpropyl)-            | 1231    | 0.019          |
| 2-Isopropyl-1-methoxy-4-methylbenzene             | 1290    | 0.088          |
| 2-Pentyl furan                                    | 1292    | 0.004          |
| 2-Octylfuran                                      | 1382    | 0.254          |
| 2-Chloro-5-methoxy-1,3-dimethylbenzene            | 1382    | 0.310          |
| Caryophyllene oxide                               | 1382    | 0.254          |

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-undecenal, and (E)-2-tetradecanal of coriander leaves and herb [19, 30]. The phytochemical study of spiny coriander shows that the 10-undecenal group (C10) 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 permissible seasonal Coriandrum.

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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.

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