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Volatiles of Black Pepper Fruits (Piper nigrum L.)

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Abstract: Black pepper (Piper nigrum) is historically one of the most important spices and herbal medicines, and is now cultivated in tropical regions worldwide. The essential oil of black pepper fruits has shown a myriad of biological activities and is a commercially important commodity. In this work, five black pepper essential oils from eastern coastal region of Madagascar and six black pepper essential oils from the Amazon region of Brazil were obtained by hydrodistillation and analyzed by gas chromatography-mass spectrometry. The major components of the essential oils were α-pinene, sabinene, β-pinene, δ-3-carene, limonene, and β-caryophyllene. A comparison of the Madagascar and Brazilian essential oils with black pepper essential oils from various geographical regions reported in the literature was carried out. A hierarchical cluster analysis using the data obtained in this study and those reported in the literature revealed four clearly defined clusters based on the relative concentrations of the major components.

Keywords: Piper nigrum; black pepper; essential oil composition; cluster analysis

1. Introduction

Genus Piper (Piperaceae) is represented by about 1500–2000 species of perennial evergreen climbing, lianescent herbs or shrubs distributed in tropical and subtropical regions. Pepper (Piper nigrum L.) is one of the oldest and most extensively used spices and traditional medicines known to mankind. The plant is believed to have originated in India and Indonesia, and has been cultivated throughout the tropical regions [1–3]. India, Brazil, Indonesia, Malaysia, Vietnam, and Sri Lanka are the major countries of P. nigrum production [3,4]. The plant can reach up to 50–60 cm in height [5] and is characterized by its simple, alternate leaves, with a few rare cases of opposite or verticillate leaves [1]. The most commonly used part of the plant is the aromatic fruit. Interestingly, white, green, and black peppers are products of the P. nigrum fruits at different ripening stages [3]. White pepper is obtained from the fully ripened fruits after removing the outer skin, green pepper is the unripe fruits, and black pepper is collected before full maturity of the fruit [1,3]. Black pepper has a stronger flavor compared to white pepper while green pepper is characterized by its fresh and herbal flavor. The alkaloid piperine is responsible for the pungent flavor of black pepper [3].

P. nigrum is well-known for its medicinal properties. Traditionally, it has been used in many Asian countries for treating indigestion, asthma, pain, respiratory tract infections, and rheumatoid arthritis [6]. It is also a stimulant, digestive, tonic, and antiseptic [5]. Black pepper essential oil (EO) showed antioxidant, carminative, larvicidal, antibacterial, and antifungal activities [2,7,8]. P. nigrum oil showed strong antibacterial activity against Acinetobacter calcoaceticus, Alcaligenes faecalis, Bacillus...
In addition, black pepper EO inhibited *Staphylococcus aureus* biofilm formation via down-regulating the expressions of the α-toxin gene (hla), the nuclease genes, and the regulatory genes [10]. It was also reported to decrease *S. aureus* virulence in *Caenorhabditis elegans* [10]. The oil prevented the formation of aflatoxin B1-DNA adduct in a microsomal enzyme-mediated reaction (in vitro) [11]. *P. nigrum* fruit oil showed some insecticide activity (contact toxicity) against *Sitophilus zeamais* (LD50 = 26.4 ± 1.5 µL/g) [1]. In patients with poor vein visibility, topical application of black pepper EO (20% in aloe vera gel) was reported to enhance vein visibility and intravenous catheter insertion [12]. Inhalation of black pepper EO was able to activate the insular or orbitofrontal cortex, which led to improved reflexive swallowing movement in older post-stroke patients with swallowing dysfunction (dysphagia) in a one-month randomized, controlled study [13]. Moreover, inhaling *P. nigrum* oil was effective in reducing smoking withdrawal symptoms including cigarette craving and anxiety [14]. Inhalation of a single drop of black pepper EO on a tissue for two minutes when craving nicotine resulted in reduced nicotine craving and increased delay time before the next tobacco use [15]. In combination with a massage, the oil can be used as a preventive treatment for cutaneous wrinkling and ageing via penetrating the skin and effectively inhibiting the activity of elastase (enzyme that degenerates dermal elastin) [16]. Compared to butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT), *P. nigrum* EO and extracts were reported to have strong in vitro and in vivo antioxidant and radical scavenging activities [2,5,8]. Oral administration of the oil for a month to mice, considerably reduced the production of super oxide radicals and increased the blood levels of superoxide dismutase, glutathione, and glutathione reductase as well as the liver levels of catalase, superoxide dismutase, glutathione, glutathione-S-transferase, and glutathione peroxidase [8]. Intraperitoneal administration of black pepper EO (500 mg/kg body weight) for five consecutive days showed strong anti-inflammatory and anti-nociceptive properties in Balb/C mice [8]. The oil inhibited the carrageenan-induced and dextran-induced acute inflammation and the formalin-induced chronic inflammation. *P. nigrum* extracts inhibited the production of pro-inflammatory nuclear factor (NF-κB), cyclooxygenase-1 (COX-1) and cyclooxygenase-2 (COX-2), and tumor cell proliferation [17]. In another randomized, double-blind, placebo-controlled study for nine weeks, inhalation of *P. nigrum* EO for 15 min showed significant analgesic activities in 54 patients with different pain types [18].

Due to the high economical and medicinal value of *P. nigrum*, it was subjected to several phytochemical studies [1,3]. Black pepper oil, which is responsible for its characteristic flavor and aroma, accounts for about 3–6% [3,8]. It ranges from colorless to greenish in color, with a spicy (peppery) scent. The oil is usually obtained from *P. nigrum* fruits by distillation, simultaneous distillation-extraction (SDE), solid phase microextraction (SPME), or supercritical fluid extraction [3,19,20]. More than a hundred compounds have been reported in black pepper oil. The oil is dominated by monoterpene hydrocarbons (47–64%) followed by sesquiterpene hydrocarbons (30–47%) [21]. In the literature, the main components frequently mentioned in *P. nigrum* oils seem to be β-caryophyllene, limonene, β-pinene, α-pinene, δ-3-carene, sabinene, and myrcene with great variations in their percentages. These variations could be attributed to differences in environmental factors, plant variety, cultivation practices, harvesting stage, and method of extraction. It may be worth mentioning that storage of ground black, green, and white pepper affects the oil composition. In the current study, we investigated the composition of the essential oils of *Piper nigrum* from the APRC collection from Madagascan east coastal region as well as essential oils from several cultivars cultivated in Pará State, Brazil.

### 2. Results and Discussion

Five *Piper nigrum* essential oils from a collection of oils from the Madagascan east coastal region, deposited with the Aromatic Plant Research Center (APRC) collection, were analyzed by gas chromatography–mass spectrometry (GC-MS). A total of 78 compounds were identified accounting...
for more than 99% of the compositions. The oils were mainly made of monoterpenic hydrocarbons (59.2–80.1%) and sesquiterpenic hydrocarbons (17.0–37.7%) while oxygenated terpenoids accounted for about 1.3–2.7%. The major components were α-pinene (5.1–28.7%), β-caryophyllene (8.7–25.6%), limonene (15.1–19.5%), β-pinene (9.1–15.3%), and δ-3-carene (9.0–12.8%; Table 1).

**Table 1.** Chemical compositions of *Piper nigrum* fruit volatile oils from the Aromatic Plant Research Center (APRC) collection.

| RI a | RI b | Compound | D170201A | FO170518Y | FO170518Z | Re180525F | DT162718 |
|------|------|----------|----------|-----------|-----------|-----------|----------|
| 921  | 921  | Tricyclene | ---      | ---       | ---       | tr c      | ---       |
| 924  | 924  | α-Thujene  | 0.1      | 0.1       | 0.2       | 0.9       | 0.6      |
| 932  | 932  | α-Pinene   | 28.7     | 12.9      | 15.2      | 5.1       | 11.1     |
| 945  | 945  | α-Fenchene  | ---      | ---       | ---       | ---       | tr       |
| 954  | 954  | Camphene   | 1.0      | 0.6       | 0.6       | 0.1       | 0.3      |
| 969  | 974  | α-Pinene   | 9.2      | 0.4       | 0.7       | 6.9       | 13.9     |
| 974  | 974  | β-Pinene   | 15.3     | 12.6      | 13.4      | 9.1       | 15.1     |
| 988  | 988  | Myrcene    | 2.6      | 2.7       | 3.0       | 2.1       | 1.3      |
| 1002 | 1002 | α-Phellorene| 2.2      | 2.5       | 3.4       | 2.3       | 0.6      |
| 1003 | 1003 | p-Mentha-1(7),8-diene | tr | --- | --- | --- | --- |
| 1008 | 1008 | β-3-Carene  | 9.0      | 11.7      | 12.8      | 11.7      | 10.4     |
| 1017 | 1017 | α-Terpine   | 0.1      | ---       | ---       | ---       | ---      |
| 1020 | 1020 | p-Cymene    | 0.3      | 0.8       | 0.4       | 1.1       | 0.3      |
| 1022 | 1022 | α-Cymene    | ---      | 0.1       | ---       | 0.1       | ---      |
| 1025 | 1025 | β-Phellorene| 0.2      | ---       | ---       | 1.4       | 0.9      |
| 1026 | 1026 | 1,8-Cineole | 0.2      | 0.3       | 0.4       | ---       | tr       |
| 1029 | 1029 | Limonene    | 19.5     | 18.2      | 18.2      | 17.4      | 15.1     |
| 1032 | 1032 | (Z)-β-Ocimene| tr | --- | --- | --- | --- |
| 1044 | 1044 | (E)-β-Ocimene| 0.4      | 0.2       | 0.3       | 0.1       | 0.1      |
| 1054 | 1054 | γ-Terpine   | 0.1      | 0.1       | 0.1       | 0.3       | 0.1      |
| 1069 | 1069 | cis-Sabinene hydrate | --- | --- | --- | 0.1 | 0.1 |
| 1086 | 1086 | Terpinolene | 0.5     | 0.8       | 0.9       | 0.5       | 0.2      |
| 1095 | 1095 | Linalool    | 0.6      | 0.4       | 0.3       | 0.5       | 0.3      |
| 1100 | 1109 | trans-Sabinene hydrate | --- | --- | --- | --- | 0.1 |
| 1135 | 1135 | trans-Pinocarveol | --- | --- | --- | --- | tr |
| 1140 | 1140 | cis-β-Terpineol | --- | 0.2       | ---       | ---       | ---      |
| 1141 | 1141 | Camphor     | 0.1      | 0.1       | tr        | ---       | ---      |
| 1174 | 1174 | Terpinen-4-ol | 0.1 | --- | --- | 0.3 | 0.2 |
| 1186 | 1186 | α-Terpineol | 0.3      | ---       | 0.2       | ---       | 0.1      |
| 1335 | 1335 | δ-Elemene   | 1.1      | 2.9       | 2.9       | 0.9       | 1.0      |
| 1338 | 1338 | α-Cubebe   | tr       | 0.1       | 0.1       | 0.3       | 0.1      |
| 1339 | 1339 | Cyclosativene 4 | 0.2      | ---       | ---       | 0.1       | 0.1      |
| 1373 | 1373 | α-Ylangene  | ---      | 0.1       | 0.1       | ---       | ---      |
| 1374 | 1374 | Isolatedene | ---      | 0.2       | 0.2       | ---       | ---      |
| 1376 | 1376 | α-Copaene  | 0.1      | 0.2       | 0.2       | 3.1       | 2.0      |
| 1387 | 1387 | β-Cubebe   | ---      | ---       | ---       | 0.2       | 0.2      |
| 1389 | 1389 | β-Elemene   | 1.0      | 1.8       | 1.4       | 1.1       | 0.2      |
| 1408 | 1408 | (Z)-β-Caryophyllene | --- | --- | --- | --- | tr |
| 1409 | 1409 | α-Gurjunene | 0.1      | 0.1       | 0.1       | 0.2       | tr      |
| 1417 | 1417 | (E)-β-Caryophyllene| 8.7      | 18.3      | 15.2      | 25.6      | 21.6     |
| 1430 | 1430 | β-Copaene  | ---      | 0.1       | ---       | 0.1       | 0.1      |
| 1436 | 1436 | γ-Elemene  | 0.1      | 0.1       | 0.1       | ---       | ---      |
| 1437 | 1437 | α-Guaiene  | 0.1      | 0.6       | 0.3       | 0.4       | tr       |
| 1448 | 1448 | cis-Murrola-3,5-diene | --- | --- | --- | --- | tr |
| 1452 | 1452 | α-Humulene | 0.9      | 1.8       | 1.3       | 1.6       | 0.7      |
| 1461 | 1461 | cis-Cadina-1(6),4-diene | --- | --- | --- | --- | tr |
| 1475 | 1475 | trans-Cadina-1(6),4-diene | tr | 0.1 | 0.4 | --- | tr |
| 1484 | 1484 | Germacrene D | 2.0    | 2.5       | 3.0       | 0.2       | 0.1      |
| 1490 | 1490 | β-Selinene | 1.3      | 2.0       | 1.9       | 1.5       | 0.1      |
| 1493 | 1493 | trans-Muurola-4(14),5-diene | --- | --- | --- | --- | 0.1 |
| 1496 | 1496 | Viridiflorene | --- | --- | 0.1 | --- | --- |
| 1498 | 1498 | α-Selinene | 1.0      | 1.5       | 1.5       | 1.3       | ---      |
| 1500 | 1500 | α-Muurolene | --- | 0.1 | 0.1 | 0.2 | 0.3 |
| 1500 | 1500 | Bicyclogermacrene | --- | --- | --- | --- | 0.3 |
Six different cultivars (“Bragantina”, “Cingapura”, “Clonada”, “Equador”, “Guajarina”, and “Uthirankota”) of *P. nigrum*, cultivated in Pará State, Brazil, were collected, hydrodistilled, and analyzed (Table 2). The oil yields (%) calculated for the cultivars (“Bragantina”, “Cingapura”, “Clonada”, “Equador”, “Guajarina”, and “Uthirankota” were 0.86%, 0.21%, 0.85%, 0.64%, 1.49%, and 1.06%, respectively.

These *P. nigrum* fruit essential oils were also rich in monoterpene hydrocarbons (76.6–89.5%) and sesquiterpene hydrocarbons (0.8–17.8%), but also had sizeable quantities of oxygenated monoterpenoids (2.2–8.2%), and oxygenated sesquiterpenoids (0.6–5.0%). The major components in the black pepper oils from Pará State were \( \beta \)-pinene (20.3–48.0%) and limonene (24.3–38.1%).

### Table 2. Chemical compositions of *Piper nigrum* fruit volatile oils cultivated in Pará State, Brazil.

| Compound                  | Bragantina | Cingapura | Clonada | Equador | Guajarina | Uthirankota |
|---------------------------|------------|-----------|---------|---------|-----------|-------------|
| \( \alpha \)-Thujene       | 0.2        | ---       | 0.2     | 0.6     | 0.7       | 1.4         |
| \( \alpha \)-Pinene        | 9.2        | 6.8       | 8.0     | 7.4     | 11.3      | 10.3        |
| Sabinene                  | ---        | 0.1       | 0.5     | ---     | ---       | ---         |
| \( \beta \)-Pinene         | 33.6       | 20.3      | 29.2    | 29.2    | 45.6      | 48.0        |
| Myrcene                   | 2.5        | 2.5       | 3.0     | 3.4     | 0.1       | ---         |
| \( \alpha \)-Phellandrene | 0.2        | 0.4       | 0.3     | 0.8     | ---       | ---         |
| \( \delta \)-3-Carene      | ---        | 14.3      | 9.3     | 4.5     | ---       | ---         |
| \( \alpha \)-Terpinene      | 0.0        | ---       | ---     | ---     | 0.7       | 1.4         |
| \( \tau \)-Cymene          | ---        | 0.1       | ---     | ---     | ---       | ---         |
| Limonene                  | 38.1       | 31.1      | 36.5    | 30.8    | 29.7      | 24.3        |
| \( E \)-\( \beta \)-Ocimene| tr         | tr        | tr      | 0.1     | ---       | 0.3         |
| \( \gamma \)-Terpinene     | 0.5        | 0.1       | 0.2     | 0.7     | 1.1       | 2.0         |
| \( cis \)-Sabinene hydrate | 0.2        | ---       | 0.1     | 0.6     | 0.4       | 0.8         |
| Terpinolene               | 0.3        | 0.8       | 0.5     | 0.4     | 0.2       | 0.4         |
| Linalool                  | 0.6        | 1.6       | 1.1     | 3.4     | 1.7       | 1.2         |
| \( cis \)-Menth-2-en-1-ol | 0.1        | ---       | 0.2     | 0.2     | 0.3       | ---         |
| \( trans \)-Menth-2-en-1-ol| 0.1        | ---       | 0.1     | 0.1     | 0.1       | 0.1         |
| Terpinen-4-ol             | 2.3        | 0.1       | 0.8     | 2.9     | 4.2       | 5.6         |
| \( \alpha \)-Terpineol     | 0.5        | 0.3       | 0.4     | 0.2     | 0.2       | 0.2         |
| Myrtenol                  | ---        | 0.1       | ---     | ---     | ---       | ---         |

*a* RI = “Retention Index” determined in reference to a homologous series of \( n \)-alkanes. *b* Retention indices from the databases [22,23]. *c* tr = “trace” (<0.05%). *d* This compound may be cyclocopacamphene, an epimer of cyclosativene.
|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| 1208 | 1214 | Linalyl formate |   | 0.1 |   |   |
| 1222 | 1227 | Nerol | 0.1 |   | 0.1 |   |
| 1334 | 1335 | δ-Elemene |   | tr | 0.4 | tr |
| 1344 | 1346 | α-Terpiny1 acetate | 0.1 |   |   |   |
| 1373 | 1374 | α-Copaene | 0.4 | 0.6 |   |   |
| 1389 | 1390 | β-Elemene |   | 0.4 | 0.4 | 0.4 |
| 1410 | 1411 | cis-Bergamotene |   |   |   | tr |
| 1416 | 1417 | (E)-β-Caryophyllene | 6.9 | 14.8 | 6.2 | 6.3 |
| 1430 | 1432 | trans-Bergamotene |   |   |   | 0.1 |
| 1431 | 1434 | (E)-β-Caryophyllene | 6.9 | 14.8 | 6.2 | 6.3 |
| 1436 | 1438 | (E)-β-Farnesene |   |   |   |   |
| 1450 | 1454 | α-Humulene | 0.4 | 0.9 | 0.5 | 0.4 |
| 1451 | 1452 | Germacrene D |   | tr |   |   |
| 1460 | 1461 | δ-3-Carene tr |   |   |   |   |
| 1490 | 1493 | α-Zingiberenol |   |   |   |   |
| 1491 | 1493 | α-Copaene | 0.4 | 0.6 |   |   |
| 1492 | 1500 | φ-Selinene | 0.1 | 0.5 | 1.0 | 0.2 |
| 1505 | 1505 | Curzerene |   |   | 0.6 |   |
| 1506 | 1506 | β-Selinene | 0.1 | 0.4 | 0.4 | 0.4 |
| 1513 | 1514 | Germacrene |   |   |   |   |
| 1521 | 1522 | δ-Cadinene |   |   |   |   |
| 1527 | 1529 | (E)-γ-Bisabolene |   |   |   | 1.2 |
| 1546 | 1548 | α-Elemol |   | tr | 0.1 | 0.2 |
| 1554 | 1559 | Germacone B |   |   | 0.1 |   |
| 1561 | 1561 | (E)-Nerolidol |   |   |   | 1.6 |
| 1577 | 1577 | Spathuleneol |   | 0.1 |   |   |
| 1582 | 1582 | Caryophyllene oxide | 0.5 | 1.0 | 0.4 | 1.6 |
| 1588 | 1596 | Fokienol |   | 0.2 |   |   |
| 1607 | 1608 | Humulene epoxide II |   |   | 0.3 |   |
| 1610 | 1612 | Ledol |   |   | tr |   |
| 1624 | 1632 | α-Acorenol |   |   |   | 0.1 |
| 1625 | 1627 | 1-sty-Cubenol | 0.2 |   |   |   |
| 1630 | 1630 | Muurola-4,10(14)-di-en-1β-ol |   | 1.1 | 0.8 |   |
| 1636 | 1639 | Caryophylla-4(12),8(13)-di-en-5β-ol |   | 0.2 |   |   |
| 1640 | 1640 | s-Murrolol | 0.3 |   |   |   |
| 1644 | 1644 | α-Muurolol (αβ-Cadinol) | 1.3 | tr | tr |   |
| 1649 | 1649 | β-Eudesmol |   |   |   | 0.1 |
| 1656 | 1658 | nor-Intermedeol |   | tr | 0.2 |   |
| 1668 | 1668 | 14-Hydroxy-β-epi-(E)-caryophyllene |   | 0.1 |   | 0.1 |
| 1677 | 1679 | Khusinol |   | 0.2 |   |   |
| 1682 | 1685 | α-Bisabolol |   | tr |   | 1.1 |
| 1714 | 1714 | 14-Hydroxy-α-humulene |   |   | 0.2 |   |
| 1727 | 1728 | iso-Longifolol |   | tr |   |   |
| 1763 | 1763 | β-Acoradienol |   |   | 0.3 |   |
| 1930 | 1930 | Musk ambrette |   |   |   |   |

- **RI** = “Retention Index” determined in reference to a homologous series of n-alkanes.  
- a Retention indices from the databases [22,23].  
- b Retention indices from the databases [22,23].  
- c tr = “trace” (<0.05%).

The oil compositions presented in this work show quantitative similarities and differences from previously published studies on black pepper oils. Bagheri and co-workers compared the composition of Malaysian pepper oils obtained by hydrodistillation and supercritical carbon dioxide extraction (SC-CO2). The hydrodistilled oil was made of β-caryophyllene (18.60%), limonene (14.95%), sabinene (13.19%), β-pinene (9.71%), δ-3-carene (8.56%), and α-pinene (7.96%) while the SC-CO2 oil had β-caryophyllene (25.38%), limonene (15.64%), sabinene (13.63%), δ-3-carene (9.34%), and β-pinene (7.27%) [5]. The major components in black pepper corn oils of Malaysian origin extracted by simultaneous distillation and extraction (SDE) were limonene (23.9–29.7%), β-pinene (15.6–19.0%), β-caryophyllene (10.3–14.0%), δ-3-carene (8.7–10.6%), and α-pinene (6.6–7.3%) while the ground
pepper oil had β-caryophyllene (38.1–63.0%), limonene (3.0–14.3%), δ-3-carene (3.0%–13.8%), and β-pinene (1.5–5.9%) [3].

Hydrodistillation of *P. nigrum* fruits grown in Cameroon produced an oil made of δ-3-carene (18.5%), limonene (14.7%), β-caryophyllene (12.8%), sabinene (11.2%), α-pinene (5.6%), and β-pinene (6.7%) [1]. α-Pinene (25.4%), limonene (21.0%), β-pinene (15.7%), and δ-3-carene (10.8%) were reported as the main constituents of *P. nigrum* fruit oil from Madagascar [24]. Interestingly, Chinese pepper EO obtained by microwave distillation and headspace solid-phase microextraction (MD-HS-SPME) has shown β-caryophyllene (23.49%), δ-3-carene (22.20%), limonene (18.68%), and β-pinene (8.92%) as the main constituents [19]. A steam-distilled oil from India had β-caryophyllene (23.98%), limonene (14.36%), α-terpinene (13.26%), caryophyllene oxide (8.04%), and α-pinene (5.0%) [8] while a hydrodistilled sample from India had β-caryophyllene (29.9%), limonene (13.2%), β-pinene (7.9%), and sabinene (5.9%) [2]. Martins and co-workers obtained *P. nigrum* EO from S. Tomé e Príncipe (hydrodistillation) and found limonene (18.8%), sabinene (16.5%), β-caryophyllene (15.1%), β-pinene (10.7%), and α-pinene (5.7%) as the main constituents [24]. The oil obtained from ground black pepper (supercritical fluid extraction, USA) was made of β-caryophyllene (21.77%), limonene (19.82%), δ-3-carene (14.34%), sabinene (11.64%), and myrcene (7.70%) [20]. Several authors have analyzed various geographical varieties of essential oils of black pepper including Thevanmundi [25], Poonjaranmuna [25], Valiakaniakadan [25], Subhakara [25], Sreekara [25], Kuching [26], Vellanamban [26], Aimpiriyan [27], Narayakodi [27], Neelamundi [27], Uthirankotta [27], and Panniyur [28].

Based on *P. nigrum* essential oil compositions, a hierarchical cluster analysis of the oils from this work (five samples from Madagascar and six samples from Pará state, Brazil) and those reported in the literature (65 samples, Table 3) was carried out. The cluster analysis revealed four clearly defined clusters (Figure 1). The cluster centroids of the major components of *P. nigrum* oils are summarized in Table 4, illustrating the chemical differences in the three classes: Class #1 (β-caryophyllene > limonene > β-pinene > sabinene > α-pinene), Class #2 (β-caryophyllene > sabinene > limonene > β-pinene > α-pinene), Class #3 (limonene > β-caryophyllene > δ-3-carene > α-pinene > β-pinene), and Class 4 (β-pinene = limonene > β-caryophyllene > α-pinene > myrcene). The first cluster was the largest representing 26 samples. APRC sample DT162718 fell in the second cluster that represents 22 samples while D170201A, FO170518Y, FO170518Z, and Re180525F fell in the third cluster that represents 17 samples. All of the Belem cultivar samples fell into the fourth cluster of 11 samples.
Table 3. Chemical compositions (major components, %) of *Piper nigrum* volatile oils reported in the literature.

| Compound | α-Thujene | α-Pinen | α-Camphene | β-Pinen | Myrcene | α-Phellandrene | β-Phellandrene | (E)-β-Ocimene | α-Carene | β-Carene | α-Limonene | β-Limonene | α-Humulene | Germaene | β-Selinene | α-Selinene | β-Elemene | δ-3-Caranene | δ-Elemene | α-β-Caryophyllene oxide |
|----------|-----------|---------|------------|---------|---------|---------------|---------------|-------------|---------|---------|------------|------------|------------|---------|-----------|-----------|---------|---------------|-----------|-----------------------------|
| Balankotta [29] | 0 | 20.0 | 0 | 0 | 0 | 13.5 | 0 | 11.7 | 8.2 | 25.2 | 0 | 0 | 0 | 0 | 0 | 7.7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Brazil, CO2 [20] | 1 | 4.1 | 0 | 11.6 | 2.6 | 7.7 | 1.9 | 14.4 | 1.8 | 19.8 | 0.4 | 0 | 0.7 | 0.4 | 0.8 | 0 | 1.3 | 1.3 | 21.8 | 0 | 1.5 | 0 | 2.5 | 3.1 | 0 | 0 | 0 | 0.5 | 0 | 0 |
| Subh-90 [26] | 0.1 | 7 | 0.2 | 0.5 | 7.6 | 7.9 | 0.1 | 19 | 23 | 22.7 | 0 | 0 | 0.1 | 0.5 | 0 | 0.1 | 0.9 | 0.2 | 7.6 | 0.1 | 0.3 | 0 | 0 | 1 | 0 | 0 | 0.1 | 0.7 | 6 |
| Subh-91 [26] | 0.1 | 3.2 | 0.2 | 0.2 | 8 | 6.7 | 3.5 | 23.4 | 0.9 | 19.5 | 0 | 0.1 | 0 | 0.6 | 0 | 0.3 | 1.7 | 0.2 | 15.5 | 0 | 0.4 | 0 | 0.1 | 0.1 | 2.8 | 0 | 0 | 0 | 0.8 | 0.4 |
| Subh-92 [26] | 0.1 | 4.7 | 0.1 | 0.2 | 9.6 | 4.3 | 3.8 | 20.8 | 0.6 | 18.3 | 0 | 0 | 0 | 0.5 | 0 | 0.1 | 1.7 | 0.1 | 21.3 | 0 | 0.4 | 0 | 0.1 | 0.1 | 3.1 | 0 | 0 | 0.8 | 3 |
| Cameroon [1] | 1.8 | 5.6 | 0.1 | 11.2 | 6.7 | 2.5 | 4.5 | 18.5 | 0.7 | 14.7 | 0 | 0.1 | 1.2 | 0.7 | 1.7 | 0.2 | 1.4 | 1.3 | 12.8 | 0 | 1.3 | 0.2 | 0 | 2.2 | tr | 0 | 0.6 | 0 | 0 |
| Sree-III [27] | tr | 4.3 | 0.2 | 0.2 | 10.2 | 5.5 | 3 | 11.1 | 0.5 | 20.1 | 0 | 0.1 | 0.1 | 0.2 | 0 | tr | 1.5 | 0.1 | 23.1 | 0 | 0.4 | 0 | tr | tr | 2.5 | 0 | 0 | 0.6 | 0.3 |
| Uthir-1st [28] | 0.2 | 14.6 | 0.4 | 0.3 | 9.3 | 4.3 | 7.4 | 8.5 | 1.3 | 19.5 | 0 | 0 | 0 | 0 | 0 | 0.1 | 0 | tr | 0.9 | 0.2 | 25.1 | 0 | tr | 0 | tr | 0 | 0 | 0 | 0.1 | tr | 0.6 |
| Kari-90 [30] | 0.1 | 5.4 | 0.2 | 0.2 | 15.2 | 0 | 3.3 | 20.3 | 0.7 | 20.1 | 0 | 0 | 0 | 0 | 0.5 | 0 | 1.9 | 0 | 0.1 | 19.8 | 0 | 0.4 | 0 | 0.1 | 0.1 | 2.5 | 0 | 0 | 0.8 | 0.4 |
| Kari-91 [30] | tr | 5 | 0.1 | 0 | 14.3 | 0.8 | 2.8 | 21 | 0.6 | 19.7 | 0 | tr | 0 | tr | 0 | 2.2 | 0 | 0 | 20.6 | 0 | tr | 0 | 0.1 | 0.1 | 2.9 | 0 | 0.2 | 0.9 | 0.4 |
| Kari-93 [30] | 0.1 | 5.3 | 0.1 | 0.6 | 14.1 | 0.9 | 2.9 | 17.8 | 0.9 | 19.6 | 0 | 0.2 | 0.2 | 0.5 | 0 | 1.5 | 0 | 0.1 | 25.6 | 0 | 0.4 | 0 | 0.1 | 0.1 | 2.7 | 0 | 0 | 0.8 | 0.5 |
| Madagascar [24] | 0 | 25.4 | 0.8 | 0 | 15.7 | 0 | 0 | 10.8 | 1 | 21 | 0 | 0 | 0 | 0 | 0.6 | 1.5 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Thom-90 [29] | 0.8 | 12.9 | 0.3 | 3.8 | 6.4 | 6.3 | 2.2 | 12.6 | 0.6 | 16.4 | 0 | 0.3 | 0.1 | 0.6 | 0 | 1.3 | 0.9 | 0 | 23.5 | 0 | tr | 0 | 0.1 | 0.3 | 0 | 0 | tr | 0 | 0.8 |
| Market [29] | 2.4 | 10 | 0 | 0 | 24.4 | 15.2 | 0 | 0 | 0 | 26.5 | 0 | 0 | 0 | 0 | 3.5 | 0 | 0 | 2.4 | 0 | 0 | 0 | 0 | 0 | 0 | 4.6 | 0 | 0 | 6.2 |
| Pann-1 [29] | 3 | 7.7 | 0 | 0 | 21.2 | 13.8 | 1.3 | 3.4 | 0 | 21.1 | 0 | 0 | 0 | 0 | 0 | 2.2 | 0 | 0 | 10.6 | 0 | 0 | 0 | 0 | 0 | 0 | 5.9 | 0 | 0 |
| Pann-5 [29] | 2.8 | 7.1 | 0 | 0 | 22.3 | 12.3 | 0 | 2.3 | 0 | 20.3 | 0 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 17.8 | 0 | 0 | 0 | 0 | 0 | 0 | 16.7 | 0 | 0 |
| Aimp-3rd [28] | 2.3 | 6.6 | 0.2 | 0 | 23.9 | 11.1 | 0.4 | 0 | 0 | 0 | 21 | 0 | 0.1 | 0.1 | 0.2 | 0 | tr | 0.4 | 1 | 16.4 | 0 | 1.1 | 0 | 0.3 | 0.7 | 0 | 0 | 0 | 9.6 | 1.2 |
|                | 0.2 | 1.4 | 19 | 2.6 | 2.2 | 10.6 | 0.5 | 29.7 | 0.3 | 0.6 | 2.1 | 0 | 1.6 | 0 | 0 | 14 | 0 | 0 | 0 | tr | 0.3 | 0.3 | 0.2 | 0.2 | 0.6 | 0.4 | 0.8 |
|----------------|-----|-----|----|-----|----|------|-----|------|----|-----|----|---|----|---|---|----|---|---|---|----|----|----|----|----|----|----|----|----|----|
| Orav 2004     | [3] |     |    |     |    |      |     |      |    |     |    |   |     |   |   |     |   |   |   |    |    |    |    |    |    |    |    |    |
| Bagheri 2014  | [5] |     |    |     |    |      |     |      |    |     |    |   |     |   |   |     |   |   |   |    |    |    |    |    |    |    |    |    |
| Thev-90       | [26]|     |    |     |    |      |     |      |    |     |    |   |     |   |   |     |   |   |   |    |    |    |    |    |    |    |    |    |
| Thev-91       | [26]|     |    |     |    |      |     |      |    |     |    |   |     |   |   |     |   |   |   |    |    |    |    |    |    |    |    |    |
| Thev-92       | [26]|     |    |     |    |      |     |      |    |     |    |   |     |   |   |     |   |   |   |    |    |    |    |    |    |    |    |    |
| Poon-90       | [26]|     |    |     |    |      |     |      |    |     |    |   |     |   |   |     |   |   |   |    |    |    |    |    |    |    |    |    |
| Poon-91       | [26]|     |    |     |    |      |     |      |    |     |    |   |     |   |   |     |   |   |   |    |    |    |    |    |    |    |    |    |
| Poon-92       | [26]|     |    |     |    |      |     |      |    |     |    |   |     |   |   |     |   |   |   |    |    |    |    |    |    |    |    |    |
| Valia-90      | [26]|     |    |     |    |      |     |      |    |     |    |   |     |   |   |     |   |   |   |    |    |    |    |    |    |    |    |    |
| Valia-91      | [26]|     |    |     |    |      |     |      |    |     |    |   |     |   |   |     |   |   |   |    |    |    |    |    |    |    |    |    |
| Valia-92      | [26]|     |    |     |    |      |     |      |    |     |    |   |     |   |   |     |   |   |   |    |    |    |    |    |    |    |    |    |
| S.Tome e      |     |     |    |     |    |      |     |      |    |     |    |   |     |   |   |     |   |   |   |    |    |    |    |    |    |    |    |    |
| Principe      |     |     |    |     |    |      |     |      |    |     |    |   |     |   |   |     |   |   |   |    |    |    |    |    |    |    |    |    |
| Market (India)| [2] |     |    |     |    |      |     |      |    |     |    |   |     |   |   |     |   |   |   |    |    |    |    |    |    |    |    |    |
| Sree-I        | [27]|     |    |     |    |      |     |      |    |     |    |   |     |   |   |     |   |   |   |    |    |    |    |    |    |    |    |    |
| Sree-II       | [27]|     |    |     |    |      |     |      |    |     |    |   |     |   |   |     |   |   |   |    |    |    |    |    |    |    |    |    |
| Kuch-I        | [27]|     |    |     |    |      |     |      |    |     |    |   |     |   |   |     |   |   |   |    |    |    |    |    |    |    |    |    |
| Kuch-II       | [27]|     |    |     |    |      |     |      |    |     |    |   |     |   |   |     |   |   |   |    |    |    |    |    |    |    |    |    |
| Vell-I        | [27]|     |    |     |    |      |     |      |    |     |    |   |     |   |   |     |   |   |   |    |    |    |    |    |    |    |    |    |
| Vell-II       | [27]|     |    |     |    |      |     |      |    |     |    |   |     |   |   |     |   |   |   |    |    |    |    |    |    |    |    |    |
| Vell-III      | [27]|     |    |     |    |      |     |      |    |     |    |   |     |   |   |     |   |   |   |    |    |    |    |    |    |    |    |    |
| Aimp-1st      | [28]|     |    |     |    |      |     |      |    |     |    |   |     |   |   |     |   |   |   |    |    |    |    |    |    |    |    |    |

**Note:** The values are represented in a tabular form with columns indicating different samples or locations, followed by numerical data in each column.
| Name       | Value  
|------------|--------|
| Aimp-2nd   | 0.5    |
| Naray-1st  | 2.7    |
| Naray-2nd  | 0.3    |
| Naray-3rd  | 1      |
| Neel-1st   | 1.6    |
| Neel-2nd   | 1      |
| Neel-3rd   | 2.2    |
| Uthir-2nd  | 0.1    |
| Kott-90    | 2.5    |
| Kott-91    | 2.4    |
| Kott-92    | 1      |
| Ott-90     | 0.7    |
| Ott-91     | 2      |
| Ott-92     | 0.6    |
| Kuth-90    | 0.6    |
| Kuth-92    | 0.2    |
| Cher-90    | 0.1    |
| Cher-91    | 3.6    |
| Cher-92    | 2      |
| Kall-90    | tr     |
| Kall-91    | 0.4    |
| Kall-93    | 0.2    |

| Name       | Value  
|------------|--------|
| Naray-1st  | 0.2    |
| Naray-2nd  | 0.3    |
| Naray-3rd  | 0.2    |
| Neel-1st   | 0.5    |
| Neel-2nd   | 0.5    |
| Neel-3rd   | 0.1    |
| Uthir-2nd  | 0.1    |
| Kott-90    | 0.1    |
| Kott-91    | 0.2    |
| Kott-92    | 0.4    |
| Ott-90     | 0.1    |
| Ott-91     | 0.4    |
| Ott-92     | 0.2    |
| Kuth-90    | 0.1    |
| Kuth-92    | 0.2    |
| Cher-90    | 0.3    |
| Cher-91    | 2      |
| Cher-92    | tr     |
| Kall-90    | 0.4    |
| Kall-91    | 0.2    |
| Kall-93    | 0.2    |

| Name       | Value  
|------------|--------|
| Naray-1st  | 0.3    |
| Naray-2nd  | 0.4    |
| Naray-3rd  | 0.2    |
| Neel-1st   | 0.5    |
| Neel-2nd   | 0.5    |
| Neel-3rd   | 0.1    |
| Uthir-2nd  | 0.1    |
| Kott-90    | 0.1    |
| Kott-91    | 0.2    |
| Kott-92    | 0.4    |
| Ott-90     | 0.1    |
| Ott-91     | 0.4    |
| Ott-92     | 0.2    |
| Kuth-90    | 0.1    |
| Kuth-92    | 0.2    |
| Cher-90    | 0.3    |
| Cher-91    | 2      |
| Cher-92    | tr     |
| Kall-90    | 0.4    |
| Kall-91    | 0.2    |
| Kall-93    | 0.2    |

| Name       | Value  
|------------|--------|
| Naray-1st  | 0.2    |
| Naray-2nd  | 0.3    |
| Naray-3rd  | 0.2    |
| Neel-1st   | 0.5    |
| Neel-2nd   | 0.5    |
| Neel-3rd   | 0.1    |
| Uthir-2nd  | 0.1    |
| Kott-90    | 0.1    |
| Kott-91    | 0.2    |
| Kott-92    | 0.4    |
| Ott-90     | 0.1    |
| Ott-91     | 0.4    |
| Ott-92     | 0.2    |
| Kuth-90    | 0.1    |
| Kuth-92    | 0.2    |
| Cher-90    | 0.3    |
| Cher-91    | 2      |
| Cher-92    | tr     |
| Kall-90    | 0.4    |
| Kall-91    | 0.2    |
| Kall-93    | 0.2    |
|                | 0.1 | 2.4 | 0.1 | 3.9 | 2   | 4   | 0.5 | 2.5 | 0.7 | 11.7 | 0   | 0   | 0.1 | 0.5 | 0   | 3.8 | 0.9 | 0   |
|----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|-----|-----|-----|-----|-----|-----|-----|-----|
| Thom-91        |     |     |     |     |     |     |     |     |     |      |     |     |     |     |     |     |     |     |
| Thom-93        |     |     |     |     |     |     |     |     |     |      |     |     |     |     |     |     |     |     |
| Arak-90        |     |     |     |     |     |     |     |     |     |      |     |     |     |     |     |     |     |     |
| Arak-91        |     |     |     |     |     |     |     |     |     |      |     |     |     |     |     |     |     |     |
| Arak-93        |     |     |     |     |     |     |     |     |     |      |     |     |     |     |     |     |     |     |

|                | 0.7 | 11.8| 0.3 | 4.1 | 7.3 | 0.4 | 0.9 | 5.4 | 0.4 | 9.4  | 0   | 0.2 | 0.1 | 0.4 | 0   | 3   | 0.7 | 0   |
|----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|-----|-----|-----|-----|-----|-----|-----|-----|
| Thom-93        |     |     |     |     |     |     |     |     |     |      |     |     |     |     |     |     |     |     |
| Thom-93        |     |     |     |     |     |     |     |     |     |      |     |     |     |     |     |     |     |     |
| Arak-90        |     |     |     |     |     |     |     |     |     |      |     |     |     |     |     |     |     |     |
| Arak-91        |     |     |     |     |     |     |     |     |     |      |     |     |     |     |     |     |     |     |
| Arak-93        |     |     |     |     |     |     |     |     |     |      |     |     |     |     |     |     |     |     |

|                | 2.2 | 6.9 | 0.1 | 20.9| 11.1| 0   | 0.3 | 0.2 | 0   | 20.4 | 0   | 0.4 | 0.2 | 0.3 | 0   | 0.1 | 0.7 | tr  |
|----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|-----|-----|-----|-----|-----|-----|-----|-----|
| Arak-90        |     |     |     |     |     |     |     |     |     |      |     |     |     |     |     |     |     |     |
| Arak-91        |     |     |     |     |     |     |     |     |     |      |     |     |     |     |     |     |     |     |
| Arak-93        |     |     |     |     |     |     |     |     |     |      |     |     |     |     |     |     |     |     |

|                | 0.4 | 4.4 | 0.6 | 5.5 | 12.5| 2.4 | 0.2 | 0.1 | 0.2 | 21.9 | 0   | 0.4 | 0.1 | 0.1 | 0   | 0.1 | 0.6 | 1   |
|----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|-----|-----|-----|-----|-----|-----|-----|-----|
| Arak-91        |     |     |     |     |     |     |     |     |     |      |     |     |     |     |     |     |     |     |
| Arak-93        |     |     |     |     |     |     |     |     |     |      |     |     |     |     |     |     |     |     |

|                | 0.6 | 2.4 | tr  | 6.3 | 6.1 | 0.2 | 0.1 | 0.4 | 0.1 | 10.3 | 0   | 0.2 | 0.1 | 0.2 | 0   | 0.6 | 1.1 | tr  |
|----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|-----|-----|-----|-----|-----|-----|-----|-----|
| Arak-93        |     |     |     |     |     |     |     |     |     |      |     |     |     |     |     |     |     |     |
| Arak-93        |     |     |     |     |     |     |     |     |     |      |     |     |     |     |     |     |     |     |
Figure 1. Dendrogram obtained from the agglomerative hierarchical cluster analysis of *Piper nigrum* oils. Entries in bold font are from this study.
Table 4. Concentration (%) of centroids used in the cluster analysis of *Piper nigrum* oils.

| Compound            | Cluster 1 | Cluster 2 | Cluster 3 | Cluster 4 |
|---------------------|-----------|-----------|-----------|-----------|
| α-Thujene           | 0.610     | 1.510     | 0.323     | 1.250     |
| α-Pinene            | 4.538     | 6.089     | 10.608    | 8.337     |
| Camphene            | 0.173     | 0.125     | 0.288     | 0.036     |
| Sabinene            | 5.892     | 19.141    | 2.179     | 0.175     |
| β-Pinene            | 6.982     | 9.621     | 10.004    | 28.796    |
| Myrcene             | 3.512     | 0.386     | 4.164     | 6.040     |
| α-Phellandrene      | 2.169     | 0.688     | 2.686     | 0.485     |
| δ-3-Carene          | 3.146     | 2.812     | 14.998    | 4.031     |
| p-Cymene            | 0.758     | 0.546     | 1.324     | 0.074     |
| Limonene            | 14.850    | 17.499    | 19.404    | 28.103    |
| β-Phellandrene      | 0.000     | 0.173     | 0.111     | 0.027     |
| (E)-β-Ocimene       | 0.588     | 0.190     | 0.111     | 0.053     |
| Terpinolene         | 0.097     | 0.184     | 0.272     | 0.302     |
| Linalool            | 0.473     | 0.398     | 0.412     | 1.083     |
| δ-Elemene           | 0.019     | 0.223     | 0.675     | 0.049     |
| α-Cubebene          | 1.661     | 0.777     | 0.477     | 0.844     |
| α-Copaene           | 0.947     | 0.777     | 0.814     | 0.132     |
| β-Elemene           | 0.148     | 0.402     | 0.515     | 0.205     |
| β-Caryophyllene     | 33.815    | 20.759    | 17.184    | 8.951     |
| α-Guaiene           | 0.183     | 0.202     | 0.088     | 0.000     |
| α-Humulene          | 0.272     | 0.523     | 0.635     | 0.299     |
| Germacrene D        | 0.012     | 0.015     | 0.465     | 0.014     |
| β-Selinene          | 0.206     | 0.295     | 0.593     | 0.223     |
| α-Selinene          | 0.483     | 0.500     | 0.674     | 0.091     |
| α-Farnesene         | 0.000     | 0.000     | 1.088     | 2.495     |
| β-Bisabolene        | 1.485     | 1.147     | 0.005     | 0.135     |
| δ-Cadinene          | 0.134     | 0.381     | 0.165     | 0.120     |
| Elemol              | 1.609     | 1.595     | 0.321     | 1.080     |
| Caryophyllene oxide | 1.923     | 1.182     | 0.863     | 1.135     |

3. Materials and Methods

3.1. Essential Oils

Volatile oils from commercial suppliers were obtained from the collections of the Aromatic Plant Research Center (APRC, Lehi, UT, USA). The samples from Pará state were provided by EMBRAPA Amazônia Oriental (Brazilian Agricultural Research Corporation) and obtained by hydrodistillation in a Clevenger apparatus (100 g, 3 h). The oils were dried over anhydrous sodium sulfate and their yields calculated from the dry weight of the plant material.

3.2. Gas Chromatographic-Mass Spectral Analysis

The essential oils obtained from APRC were analyzed by gas chromatography-mass spectrometry (GC-MS) using a Shimadzu GCMS-QP2010 Ultra operated in the electron impact (EI) mode (electron energy = 70 eV), scan range = 40–400 atomic mass units, scan rate = 3.0 scans/s, and GC-MS solution software. The GC column was a ZB-5 fused silica capillary column with a (5% phenyl)-polymethylsiloxane stationary phase and a film thickness of 0.25 μm, a length of 30 m, and an internal diameter of 0.25 mm. The carrier gas was helium with a column head pressure of 552 kPa and flow rate of 1.37 mL/min. The injector temperature was 250 °C and the ion source temperature was 200 °C. The GC oven temperature was programmed for 50 °C initial temperature, then
temperature was increased at a rate of 2 °C/min to 260 °C. A 7% w/v solution of the sample was prepared in dichloromethane and 0.1 µL was injected with a splitting mode (30:1).

Qualitative analysis of the Belém samples was carried out by gas chromatography-mass spectrometry (GC-MS) (Shimadzu QP2010 plus instrument, Shimadzu Scientific Instruments, Columbia, MD, USA) under the following conditions: Rtx-5MS silica capillary column (30 m × 0.25 mm film thickness, Phenomenex, Torrance, CA, USA); programmed temperature, 60–240 °C (3 °C/min); injector temperature, 200 °C; carrier gas, helium, adjusted to a linear velocity of 1.2 mL/min; injection type, splitless; split flow was adjusted to yield a 20:1 ratio; septum sweep was a constant 10 mL/min; EIMS, electron energy, 70 eV; and temperature of the ion source and connection parts, 200 °C. The retention indices were calculated for all the volatile constituents using a homologous series of n-alkanes (C8–C32, Sigma-Aldrich). Identification of the oil components was based on their retention indices and by comparison of their mass spectral fragmentation patterns with those reported in the literature [23], and our own in-house library [24]. The component percentages are based on peak integrations without standardization.

3.3. Hierarchical Cluster Analysis

_P. nigrum_ oils obtained from this work as well as the published literature were used in the cluster analysis. The essential oil compositions were treated as operational taxonomic units (OTUs), and the concentrations (percentages) of the major components (α-thujene, α-pinene, camphene, sabinene, β-pinene, myrcene, α-phellandrene, δ-3-carene, p-cymene, limonene, β-phellandrene, (E)-β-ocimene, terpinolene, linalool, δ-elemene, α-cubebene, α-copaene, β-elemene, β-caryophyllene, α-guaiene, α-humulene, germacrene D, β-selinene, α-selinene, α-farnesene, β-bisabolene, δ-cadinene, elemol, and caryophyllene oxide) were used to determine the chemical associations between the essential oils using agglomerative hierarchical cluster (AHC) analysis using XLSTAT Premium, version 2018.5.53172 (Addinsoft, Paris, France). Dissimilarity was determined using Euclidean distance, and clustering was defined using Ward’s method.

4. Conclusion

The essential oils of black pepper have been analyzed by GC-MS. The oils were dominated by monoterpene hydrocarbons. Black pepper oils from various geographical locations have shown qualitative similarities with differences in the concentrations of their major components. β-Caryophyllene, limonene, β-pinene, α-pinene, δ-3-carene, sabinene, and myrcene were the main components of _P. nigrum_ oil. The cluster analysis revealed four clearly defined clusters for _P. nigrum_.

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