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Chemical Compositions and Antioxidant Activities of Indonesian *Citrus* Essential Oils and Their Elucidation Using Principal Component Analysis

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Abstract: *Citrus* essential oils (EOs) have various bioactivities like antioxidants, with many applications. Antioxidant activities depend on the chemical compositions of the EOs, which are affected by climate, soil, and geographical region. Thus, investigations on chemical compositions and antioxidant activities of *Citrus* EOs in different countries are valuable. In this study, we distilled EOs from peels of Indonesian-grown *Citrus*, including *C. nobilis, C. limon, C. aurantifolia, C. amblycarpa*, and *Citrus spp*. Chemical compositions of EOs were analyzed using Gas Chromatography-Mass Spectrometer (GC-MS), whereas the antioxidant activities were determined by employing 2,2-diphenyl-2-picrylhydrazyl (DPPH) method. Furthermore, principal component analysis (PCA) was applied to elucidate the main contributing compounds for antioxidant activity. The results show that all EOs possess unique chemical characteristics, with limonene as the majority constituent. For antioxidant activities, *C. limon* and *C. amblycarpa* EOs are the two strongest, IC_{50} values below 7.00 μL/mL. PCA approach suggests that *γ*-terpinene mainly contributes to the high antioxidant activities of *C. limon* and *C. amblycarpa*. Moreover, *o*-cymene, thymol, *p*-cymene, and *α*-pharnesene may also be responsible for the antioxidant activity of *C. limon* EO. These results are valuable information for the applications of *Citrus* EOs as antioxidant sources.

Keywords: chemical composition; antioxidant; *Citrus*; essential oils; Principal Component Analysis.

1. Introduction

Citrus is a prominent genus in the Rutaceae family, which consists of 154 genus and 2100 species. *Citrus* plants widely spread around the globe dan can grow in tropical and subtropical zones [1,2]. Common species from this genus are *Citrus aurantifolia, C. nobilis, C. amblycarpa, C. limon (C. limonia, C. limonum), C. aurantium sp. C. aurantium, C. sinensis, C. reticulata, C. paradise, C. bergamia*, and *C. medica* [3]. The consumption of *Citrus* fruits is extensive due to their delicious tastes and beneficial metabolites such as coumarins, flavonoids, limonoids, pectin carotenoids, as well as vitamins A, C, and E. Those metabolites possess a variety of biological activities, including anti-inflammatory, antioxidant, antimutagen, anticarcinogen, and antiaging [1]. Therefore, *Citrus* fruits have many applications in the fields of food, health, and cosmetics [3].

The *Citrus* peels contain glands of essential oils (EOs) in their flavedo and cuticula [4,5]. The EOs have various unique aromas that depend on their chemical compositions [6]. Citrus EOs mainly consist of monoterpenes and sesquiterpenes [5]. One example is Limonene, a monoterpene which constitutes around 65.3 to 95.9% *Citrus* EOs [7]. Other compounds are *β*-pinene, *α*-terpineol,

terpinen-4-ol, β-myrcene, γ-terpinene, β-phellandrene, *o*-cymene, and citral. These compounds are variables that contribute to the characteristics and bioactivities of *Citrus* EOs [8].

Citrus EOs have diverse bioactivities, such as antioxidant [6,7]. Antioxidant protects cellular structure and function by scavenging free radicals, inhibiting lipid peroxidation, and preventing other oxidative degradations [1]. Therefore, compounds with antioxidant bioactivities have been widely used as additives in food products [9] and antiaging in cosmetics [3].

Several research groups have performed studies regarding characterizations and antioxidant activities of different *Citrus* EOs [10–12]. Moosayv and coworkers [12] analyzed the EO of *C. limon* grown in Iran and found four main compounds: limonene (46.93%), terpinene (16.89%), tricyclene (6.67%), and β-pinene (4.69%). Gursoy and colleagues [11] reported that the EO from *C. nobilis* peels contains limonene (76.77%), γ-terpinene (8.24%), linalool (3.01%), and myrcene (2.38%). They suggested limonene as the compound mainly responsible for the antioxidant activity of *C. nobilis* EO. Meanwhile, Frassinetti and coworkers [10] found that among commercial Citrus EOs in Italy, *C. limon* EO is the most active antioxidant.

Chemical compositions of *Citrus* EOs in terms of qualitative and quantitative are affected by climate, soil, and geographical region [13]. Meanwhile, chemical compositions of *Citrus* EOs determine their antioxidant activities [14]. Thus, investigating chemical compositions and antioxidant activities of *Citrus* EOs from other countries are important research topics. In this present work, we distilled *Citrus* EOs from peels of *C. nobilis, C. limon, C. aurantifolia, C. amblycarpa*, and *Citrus spp.* grown in Indonesia. Chemical compositions of *Citrus* EOs were analyzed using Gas Chromatography-Mass Spectrometer (GC-MS). Antioxidant activities of all EOs were also determined using 2,2-diphenyl-2-picrylhydrazyl (DPPH) method. We applied principal component analysis (PCA) to elucidate the responsible secondary metabolites for the antioxidant activity. PCA is a powerful tool for exploratory data analysis and has vital roles in many fields, such as drug design [15], chemotaxonomy [16], and metabolite profiling [17]. This study is essential in providing valuable information about the antioxidant activities of various *Citrus* EOs and the responsible secondary metabolites. This study will help the application of *Citrus* EOs in many fields, for example, health, food, functional fabric, and cosmetics.

2. Results and Discussion

2.1. Yields of Citrus Essential Oils

In this present work, we have distilled EOs from five *Citrus* species. The obtained *Citrus* EOs are clear liquids and have pale-yellow colors with fresh aromas. The resulting EO yields vary among species, ranging from 0.34-3.70%. The highest EO yield was acquired from the peel of *C. nobilis* (3.70%), followed by *C. limon* (0.85%), *C. aurantifolia* (0.78%), *C. amblycarpa* (0.65%), and *Citrus spp.* (0.34%).

Table 1. Yields of EOs from peels of five different Citrus species.

No.	Citrus Peel	Peel Weight (g)	EO Weight (g)	Yield (%)
1.	*C. nobilis*	500	18.5	3.70
2.	*C. limon*	500	4.25	0.85
3.	*C. aurantifolia*	500	3.90	0.78
4.	*C. amblycarpa*	500	3.25	0.65
5.	*Citrus spp.*	500	1.70	0.34

Our results are slightly higher than those reported by others [5,18], where yields of EOs are usually between 0.2 and 2.3%. The EO yields depend on plant genetics, climate, soil, geographical location, and storage period [19]. Therefore, the amount of EO obtained may vary even for the same species.

2.2. Chemical Composition

Table 2 shows that the five *Citrus* EOs have different chemical compositions in terms of qualitative and quantitative (see Figure S1 for the chemical structures). The *Citrus* EOs contain monoterpene, monoterpenoid, sesquiterpene, and sesquiterpenoid types of secondary metabolites. These secondary metabolite classes sparsely distribute among the five *Citrus* EOs. Monoterpenes are the dominating secondary metabolites in *Citrus* EOs, where limonene is the main component. Limonene constitutes 40 to 67% of chemical compositions of *Citrus* EOs. Our result is consistent with the literature that limonene is the most abundant secondary metabolite in Citrus EOs [9]. The highest limonene level presents in *Citrus spp.* (67.76%), followed by *C. limon* (54.62%), *C. nobilis* (50.06%), *C. amblycarpa* (42.23%), and *C. aurantifolia (*40.84%).

Table 2. Chemical composition of secondary metabolites in the EOs of five *Citrus* species.

Secondary Metabolite	Percentage in EO (%) [1]				
	C. aurantifolia	*C. nobilis*	*C. limon*	*C. amblycarpa*	*Citrus spp.*
Monoterpenes					
o-Cymene	0.67	-	4.66	-	-
p-Cymene	-	-	1.46	-	-
α–Pinene	1.60	-	-	0.52	-
Camphene	0.33	-	-	0.57	-
β-Pinene	0.81	3.69	0.29	5.30	-
Limonene	40.84	50.06	54.62	42.23	67.76
β–Phellandrene	0.36	0.70	-	1.10	-
γ–Terpinene	0.80	-	4.30	2.50	-
(+)-4-Carene	1.21	-	-	-	-
2-Carene	0.20	-	0.42	1.21	-
γ–Elemene	0.46	-	-	-	-
β-Myrcene	17.75	4.57	0.59	-	0.72
β–Ocimene	0.63	1.37	-	-	0.70
Monoterpenoids					
Thymol	-	-	8.76	-	-
Terpinen-4-ol	1.34	1.51	1.14	11.63	-
α–Terpineol	3.54	4.05	3.65	4.83	-
trans-Carveol	-	0.75	-	-	-
Limonene oxide	-	-	-	-	1.53
Citral	1.00	-	-	-	6.15
Citronellal	-	2.18	-	-	-
Citronellol	-	0.70	-	4.25	-
Geraniol	-	0.82	-	-	-
Sesquiterpenes					
α -Pharnesene	-	-	0.34	-	-
β–Bisabolene	1.47	-	-	2.86	-
Sesquiterpenoid					
Caryophyllene	1.44	-	-	-	-

[1] The levels of secondary metabolites are originated from the corresponding peak area percentages in GC chromatograms, which also consist of primary metabolite peaks (data not shown).

Every EO has its chemical composition characteristics. *C. aurantifolia* EO contains the most diverse secondary metabolites (Table 2). Based on our results, the EO of *C. aurantifolia* is characterized by seventeen secondary metabolites, which are dominated by monoterpenes as many as twelve compounds. Additionally, the EO has secondary metabolites exclusive to *C. aurantifolia*. These consist of γ–elemene and (+)-4-carene monoterpenes, as well as a caryophyllene sesquiterpenoid. The EO of *C. nobilis* contains monoterpene and monoterpenoid secondary metabolites, which spread evenly (Table 2). The EO has unique compounds: *trans*-carveol, citronellal, and geraniol. Like *C. aurantifolia*, *C. limon* produced EO with chemical composition dominated by monoterpenes. The EO contains three aromatic compounds, including o-cymene, p-cymene, and thymol. The two last compounds and α-pharnesene are exclusive to *C. limon* EO. Likewise, *C. amblycarpa* EO contains monoterpenes as the main types of secondary metabolites. The EO has a relatively high content of terpinen-4-ol and citronellol compared to the other *Citrus* EOs (Table 2). Meanwhile, *Citrus spp.* EO has the lowest diversity of secondary metabolites. Only four secondary metabolites constitute *Citrus spp.* EO. They are limonene, β-myrcene, β–ocimene, limonene oxide, and citral. The levels of limonene and citral are the highest in *Citrus spp.* EO. Furthermore, limonene oxide is limited to this EO.

2.3. Antioxidant Activity

Antioxidant activities of *Citrus* EOs are represented by the percentage of free radical scavenging (%) (Figure S2) and the concentration of 50% scavenging (Table 2). Each EO exhibits a different inhibition profile in scavenging DPPH free radicals (Figure S2). The EO of *C. limon* shows the highest antioxidant activity with IC_{50} of 4.25 ± 0.08 μL/mL (Table 2), consistent with the work published by Frassinetti and colleagues [10]. The antioxidant activity of *C. limon* EO even higher than that of ascorbic acid. In the second place, *C. amblycarpa* shows an IC_{50} value of 6.30 ± 0.04 μL/mL. The EOs of *C. aurantifolia* and *Citrus spp.* display similar calculated IC_{50} values, 12.85 ± 0.20 and 13.29 ± 0.04 μL/mL, respectively. Meanwhile, the EO of *C. nobilis* possesses the weakest antioxidant activity with an IC_{50} value of 15.83 ± 0.04 μL/mL. These different antioxidant activities of EOs may be due to their chemical composition characteristics.

Table 2. Antioxidant activities of EOs from five *Citrus* species.

Citrus	IC_{50} (μL/mL)
Ascorbic Acid	5.28 ± 0.02
C. limon	4.25 ± 0.08
C. amblycarpa	6.30 ± 0.04
C. aurantifolia	12.85 ± 0.20
Citrus spp.	13.29 ± 0.04
C. nobilis	15.83 ± 0.04

2.4. Principal Component Analysis

As discussed above, we have identified twenty-five secondary metabolites, which are sparsely distributed among the EOs from five different *Citrus* species. Those secondary metabolite profiles may contain redundant information, which raises an issue in elucidating antioxidant activities of *Citrus* EOs. Therefore, we transformed Table 1 into a matrix (Table S1) and performed a PCA approach. Through linear combinations, PCA transformed correlated/uncorrelated descriptors, including twenty-five secondary metabolites. Subsequently, the essential information was extracted into only four uncorrelated variables or principal components (PCs) (Figures 1 and 2).

As portrayed in Figure 1, PC1 is important for camphene, limonene, β-phellandrene, terpinen-4-ol, and β-bisabolene. PC1 has representation qualities above 70% for these secondary metabolites (Table S2). Additionally, β-pinene, α-terpineol, 2-carene, and citronellol are represented around 60% by PC1. The importance of PC2 is very high for γ-terpinene, above 94%, while for o-cymene 63%. For β-ocimene, thymol, p-cymene, and α-pharnesene, the representation qualities of PC2 are around 70%.

Thus, the fifteen secondary metabolites, which are shaded by gradient colors of dark blue in Figure 1, have good representations on PC1 and 2. Meanwhile, PC3 is important for (+)-4-carene, caryophyllene, and γ-elemene, with representation qualities of 71%. For α-pinene and β-myrcene, the representation qualities of PC3 are 58 and 51%, respectively.
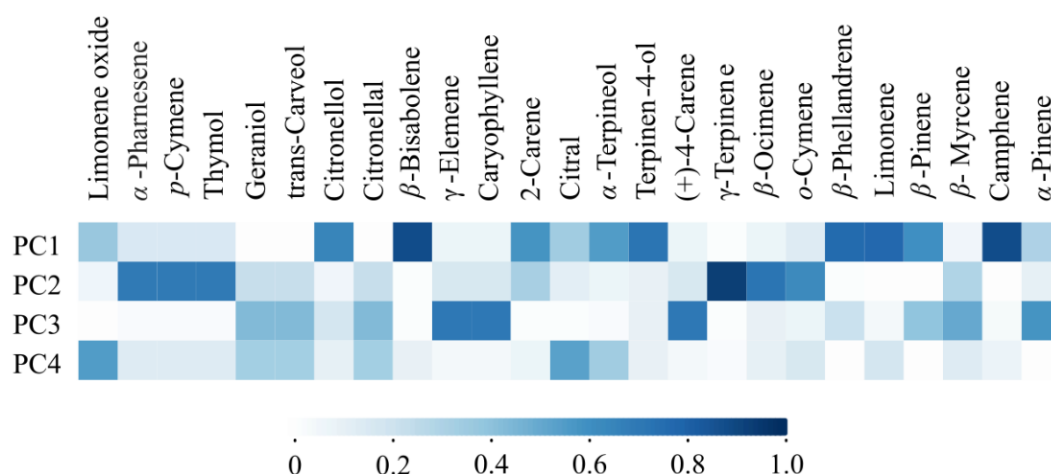

Figure 1. Representation quality heatmap of the descriptors on the PCs. The gradient colors of blue denote scales of representation quality. Representation quality refers to the importance of a principal component for a given variable.

According to Figure 2.a., the proportion of variance explained by each PC is not highly different. PC1 captured 33.8% of the total variance, while PC2 and 3 explain 26.9 and 23.1%, respectively. The rest variance is described as much as 16.3% by PC4. Combination of PC1 and 2 only explain 60.7% of the total variance (Figure 2.b). Thus, we may need at least three PCs to explain more than 80% of the total variance contributed by secondary metabolite descriptors.
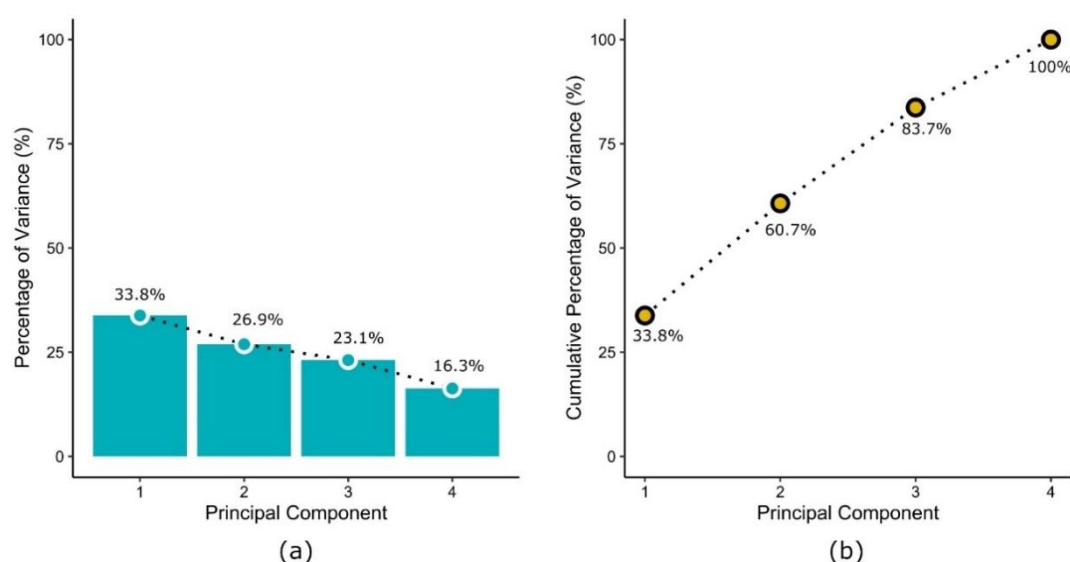

Figure 2. (a) Scree and (b) cumulative plots of principal component analysis of five *Citrus* essential oils.

Intriguingly, the score plot on the coordinate system of PC1 and 2 revealed an informative result (Figure 3.a). In such a coordinate system, *Citrus* EOs spread according to their antioxidant activities. The EOs with IC_{50} above 12 ppm (Table S3) cluster in the third and fourth quadrants. On the other hand, the EOs with IC_{50} around 5 ppm are on the opposing side. The score plot (Figure 3.a) displays

that the PC2 alone, which explains 26.9% of the total variance, can separate the essential oils based on their antioxidant activities. Nevertheless, the presence of PC1 assists in further separation of *Citrus spp.*, *C. nobilis,* and *C. aurantifolia*. Furthermore, PC1 also helps the analysis through a biplot (Figure 3.b).

The biplot (Figure 3.b) explains the difference between *Citrus* EOs based on their secondary metabolites. As an example, *C. limon* EO is characterized by thymol, *o*-cymene, *p*-cymene, *α*-pharnesene, and *γ*-terpinene. Thymol, *p*-cymene, and *α*-pharnesene present only in *C. limon* EO, whereas the levels of *o*-cymene and *γ*-terpinene in the EO are the highest among other *Citrus* EO. For *C. amblycarpa* EO, camphene, terpinen-4-ol, *α*-terpineol, 2-carene, *β*-bisabolene, and citronellol describe the oil characteristic. In *C. amblycarpa* EO, the levels of those secondary metabolites are relatively higher than in other *Citrus* EOs. Interestingly, the biplot result supports the chemical composition characteristics of EOs in the sub-section on *Chemical Composition*.
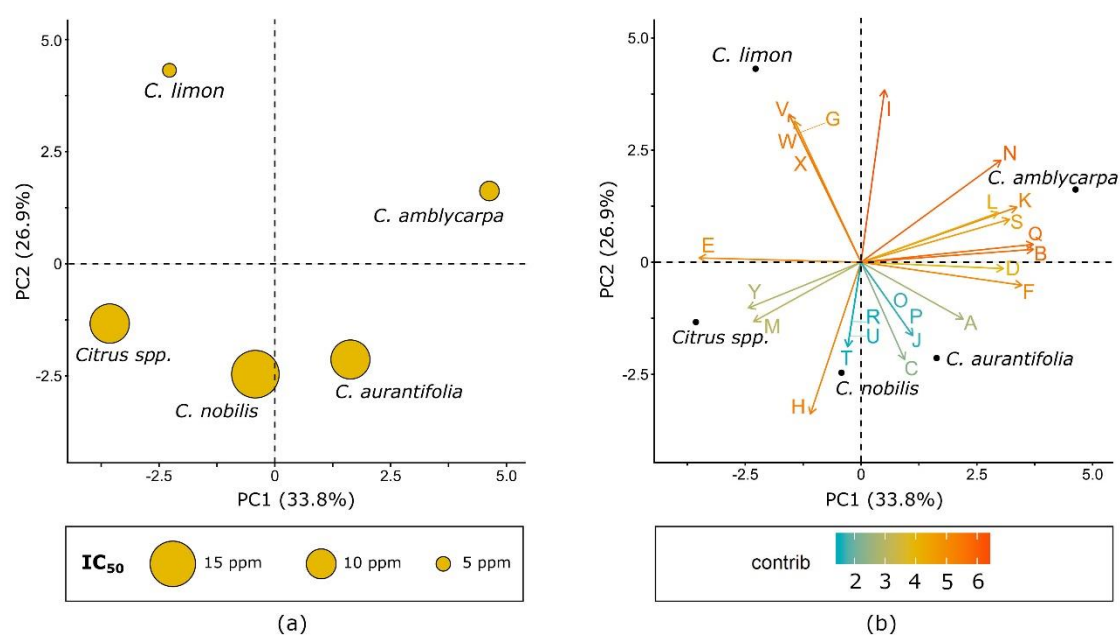

Figure 3. (a) Individual plot and (b) biplot of EOs from five citrus species in the coordinate system of PC1 and 2. The size of circle in the individual plot represents the value of IC$_{50}$. The color gradient and arrow length of the secondary metabolite descriptors in the biplot indicates their importance in the coordinate system of PC1 and PC2. In the biplot, secondary metabolites are coded by alphabetic letters; A: *α*-Pinene; B: Camphene; C: *β*-Myrcene; D: *β*-Pinene; E: Limonene; F: β-Phellandrene; G: *o*-Cymene; H: *β*-Ocimene; I: *γ*-Terpinene; J: (+)-4-Carene; K: Terpinen-4-ol; L: α-Terpineol; M: Citral; N: 2-Carene; O: Caryophyllene; P: *γ*-Elemene; Q: *β*-Bisabolene; R: Citronellal; S: Citronellol; T: *trans*-Carveol; U: Geraniol; V: Thymol; W: *p*-Cymene; X: *α*-Pharnesene; Y: Limonene oxide.

As discussed above regarding the score plot (Figure 3.a.), only PC2 can separate *Citrus* EOs on the factor map based on antioxidant activity (Figure S1). Therefore, in the context of antioxidant activity, we only consider secondary metabolites that are highly represented by PC2 (Figure 1). These secondary metabolites are *γ*-terpinene, *β*-ocimene, thymol, *o*-cymene, *p*-cymene, and *α*-pharnesene. Not surprisingly, *C. limon* EO possesses the highest antioxidant activity among others since its character is determined by *γ*-terpinene, *o*-cymene, thymol, *p*-cymene, and *α*-pharnesene. The last three secondary metabolites present only in *C. limon* EO. Additionally, the levels of *γ*-terpinene (4.30%) and *o*-cymene (4.66%) in *C. limon* EO are the highest, among others. In the EOs with low antioxidant activities, *γ*-terpinene and *o*-cymene are absent, or the levels are low (Table S1 and S3). Interestingly, the EO of *C. amblycarpa* with the second-highest antioxidant activity does not have *o*-cymene, thymol, *p*-cymene, and *α*-pharnesene but contains a considerable amount of *γ*-terpinene

(2.50%). Hence, γ-terpinene may mainly contribute to the high antioxidant activities of *C. limon* and *C. amblycarpa*. For *C. limon* EO, its high antioxidant activity may also be supported by *o*-cymene, thymol, *p*-cymene, and α-pharnesene.

2.5. Chemical Structures of the Antioxidants

Our study using PCA suggests that thymol, *o*-cymene, *p*-cymene, β-ocimene, α-pharnesene, γ-terpinene (Figure 4) are the metabolites contributing to the antioxidant activities, particularly for *C. limon* EO. Thymol has antioxidant activity because it is a phenolic compound. Its hydroxyl group inhibits DPPH• radicals through hydrogen atom transfer (HAT). After transferring its hydrogen atom, thymol becomes a stable radical (thymol•) and reacts with other radicals to form DPPH-thymol or thymol-thymol [20].
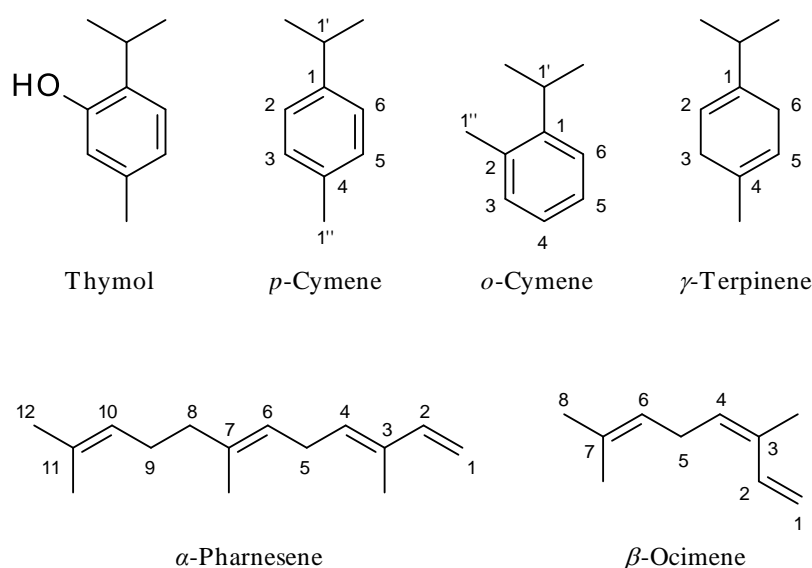

Figure 4. Two-dimensional structures of secondary metabolites responsible to antioxidant activities of EOs according to PCA.

Antioxidant activities of *p*-cymene and *o*-cymene come from their benzylic hydrogen atoms at two different positions, carbon 1' and 1" (Figure 4) [21]. The abstraction of the benzylic hydrogen atoms quenches free radicals, while the secondary metabolites turn into stable radical molecules. In both α-pharnesene and β-ocimene, hydrogen atom transfer from carbon 5 to DPPH• molecules yield stable radicals. The stabilization comes from conjugated double bonds in α-pharnesene and β-ocimene structures, at carbon 1 and 3.

γ-Terpinene has antioxidant activity even it does not have conjugated double bonds [22]. It is a strong antioxidant similar to α-tocopherol, a well-known antioxidant [23]. Liu and Li [24] reported that γ-terpinene can directly scavenge free radical by donating its hydrogen atom at the allylic position, particularly carbon 3 and 6 (Figure 6). Additionally, γ-terpinene has been reported to retard linoleic acid peroxidation [22]. Such activity undergoes through a rapid cross-reaction between hydroperoxyl (HOO•) and linoleylperoxyl (LOO•) which terminates free radical chain reaction. Moreover, the retardation of linoleic acid peroxidation converts γ-terpinene to *p*-cymene, an antioxidant.

3. Materials and Methods

3.1. Citrus Essential Oil Preparation and Gas Chromatography-Mass Spectrophotometry

Fruits of *C. aurantifolia*, *C. nobilis*, *C. limon*, *C. amblycarpa*, and *Citrus spp.* were collected from Caringin Central Market, Bandung, West Java, Indonesia during July to August 2018. The peels of *C. aurantifolia*, *C. nobilis*, *C. limon*, *C. amblycarpa*, and *Citrus spp.* were separately cleaned and cut into ± 2

cm. Each sample of Citrus peel (500 g) was subjected into a Clevenger-type hydrodistillation for 8 hours. The obtained EOs were dried using anhydrous sodium sulfate and stored in airtight containers at 4 °C before gas chromatography-mass spectrometry (GC-MS) analysis.

3.2. Gas Chromatography-Mass Spectrophotometry (GC-MS)

Chemical compositions of EOs were analyzed using GC-MS (Agilent GC Type 7890A amd MS Type 5975C). The analysis utilized DB 35MS column with length of 35 m, internal diameter of 0.25 mm, and film thickness of 0.25 μm. Nitrogen was used as the carrier gas at a flow rate of 1 mL/min. Every citrus EO was diluted in n-hexane to achieve concentration of 0.5% (v/v). Each one microliter EO solution was loaded to an injector with a temperature of 250 °C. The column was initially held as 50 °C for 1 minute and increased to 250 °C with a heating ramp of 3.5 °C/min.

3.3. Antioxidant Activity Assay

Antioxidant activities of *Citrus* EOs were determined using 2,2-diphenyl-2-picrylhydrazyl (DPPH) assay with a modification [25]. Briefly, 0.1 mL EOs at different concentrations (Table S3) were mixed with 2 mL DPPH (0.21 mM in ethanol 95%), in duplicate, and incubated in the dark for 60 min. After incubation, the absorbance was measured at 517 nm. As the control, ethanol was used instead of EO. Ascorbic acid was employed as the standard antioxidant compound. DPPH free radical scavenging activity was computed by utilizing the equation below:

$$\%DPPH - scavenging\ activity = \frac{A_{control} - A_{sample}}{A_{control}} \times 100\% \tag{1}$$

$A_{control}$ denotes control absorbance, whereas A_{sample} is sample absorbance. Antioxidant activity was also expressed as IC_{50} or concentration of EO (mg/mL) required to inhibit 50% DPPH. IC_{50} was determined from the plot % DPPH scavenging activity *vs*. EO concentration.

3.4. Principal Component Analysis

Peaks of secondary metabolites, from the GC-MS chromatogram of every citrus essential oil, were manually curated and assigned to a matrix (row *i*, column *k*) as listed in Table S1. The citrus species were treated as observation (*i*), whereas the secondary metabolites such as *α*-pinene and camphene were descriptors (*k*). Two types of preprocessing were performed to the matrix. The first one was mean centering to retain only the informative variation. The second one was scaling since levels of secondary metabolites in five citrus essential oils displaying different scales.

The matrix was subjected to an orthogonal linear transformation to generate a new coordinate system of principal components [26]. On the axis of rank *s*, F_s (resp. G_s) indicates the coordinate vectors of the citrus species (resp. descriptors). They can be expressed as:

$$F_s(i) = \frac{1}{\sqrt{\lambda_s}} \sum_k x_{ik}\, m_k G_s(k) \tag{2}$$

$$G_s(k) = \frac{1}{\sqrt{\lambda_s}} \sum_k x_{ik}\, p_i F_s(i) \tag{3}$$

$F_s(i)$ represents the coordinate of each *i* on the axis *s*, whereas $G_s(k)$ is the coordinate of descriptor *k* on the axis *s*. Notation *s* the eigenvalue corresponds to the axis *s*, m_k the weight corresponds to descriptor *k*, p_i is the weight corresponding to each i, x_{ik} is the general term of the matrix (row *i*, column *k*).

Computations and data visualizations were performed in the R programming language environment [27]. PCA was computed using *FactorMineR* [26]. Subsequently, the results were visualized using *factoextra* [28] or *ggplot2* [29].

4. Conclusions

In this study, we distilled EOs from the peels of *C. nobilis*, *C. limon*, *C. aurantifolia*, *C. amblycarpa*, and *Citrus spp.* grown in Indonesia. All EOs contain limonene as the main constituent, ranging from 40 to 67%. Additionally, each EO exhibits individual chemical characteristics. Caryophyllene, (+)-4-carene, and c-elemene only present in *C. aurantifolia* EO, whereas citronellal, trans-carveol, and geraniol are unique metabolites in *C. nobilis* EO. Thymol, *p*-cymene, and α-pharnesene are exclusive in the EO of *C. limon*. Meanwhile, limonene oxide only presents in the EO of *Citrus spp.*

The antioxidant assay using DPPH method showed *C. limon* EO possessing the strongest free-radical-scavenging activity (IC_{50} of 4.25 ± 0.08 μL/mL), followed by *C. amblycarpa* (6.30 ± 0.04 μL/mL). Meanwhile, EOs of *C. aurantifolia*, *Citrus spp.*, and *C. nobilis* exhibit IC_{50} values above 12.85 μL/mL. Exploratory data analysis using PCA lead to secondary metabolites that may mainly contribute to antioxidant activities of *Citrus* EOs. These metabolites are thymol, *o*-cymene, *p*-cymene, β-ocimene, α-pharnesene, γ-terpinene. Monoterpene of γ-terpinene may play a key role to the high antioxidant activities of *C. limon* and *C. amblycarpa* EOs. For *C. limon* EO, its high antioxidant activity may also be contributed by *o*-cymene, thymol, *p*-cymene, and α-pharnesene.

In summary, this study provides valuable data regarding antioxidant activities of five *Citrus* EOs grown in Indonesia and the responsible secondary metabolites. The information will guide the implementations of *Citrus* EOs as antioxidant sources in many fields, ranging from food, cosmetics, health to functional fabric.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, Figure S1: Chemical structures of secondary metabolites in essential oils (EOs) of five Indonesian-grown *Citrus*, Figure S2: Percentage of free-radical scavenging activity of five Indonesian-grown *Citrus*, Figure S3: Score plots on the coordinate systems of all PC combinations, Table S1: A matrix containing five rows of Citrus species and twenty-five columns of secondary metabolites, Table S2: Representation quality of every descriptor on each PC.

Abbreviations

EO	Essential Oil
DPPH	diphenyl-2-picrylhydrazyl
GC-MS	Gas Chromatography-Mass Spectrometer
IC_{50}	Inhibition Concentration 50; concentration of EO (mg/mL) required to inhibit 50% DPPH.
PCA	Principal Component Analysis
PC	Principal Component

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Sample Availability: Samples of *Citrus* EOs are available from the authors.