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Comparison of Major Volatile Compounds in Three Varieties of Ginger Grown in Indonesia using Solid Phase Micro Extraction Gas Chromatography/Mass Spectroscopy Followed by Electronic Nose Based on Metal Oxide Semiconductor Gas Sensor

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Abstract: Solid Phase Micro Extraction-Gas Chromatography/Mass Spectroscopy (SPME-GC/MS) was employed to identify major compounds in three varieties of ginger grown in Indonesia, namely: small-white ginger (SWG), big-white ginger (BWG), and red ginger (RG). SWG was dominated by β-sesquiphellandrene and α-farnesene. The major chemical compounds identified in BWG were dominated by: α-zingiberene, cedren-13-ol, 8-, β-bisabolene, and neral, while curcumene, neral, α-zingiberene, citral, and geraniol were most dominant in RG. Sensory analysis using electronic nose (e-nose) based on metal oxide semiconductor (MOS) gas sensor was also employed to measure the sensory response of these gingers. Principal component analysis (PCA) of feature e-nose response showed that the feature response of three gingers can be separated. The score plot in the PC_1-PC_2 coordinate of PCA obtained 89.30 % of variance at two principal components. PC_1 contributed 58.30 % of the variance, while PC_2 contributed 31.00 %. Furthermore, hierarchical cluster analysis (HCA) of feature response of three gingers indicated that the similarity level between BWG and RG is almost 36.12 %, due to the presence of α-zingiberene and neral, that was identified more than 10 % both in BWG and RG.

Keywords: Indonesia ginger, SPME-GC/MS, E-nose, Principal component analysis, Hierarchical cluster analysis.

1. Introduction

Ginger (*Zingiber officinale Roscoe*), is one of the most well-known herbal medicines in Indonesia. This herbal is commonly used as raw material for traditional beverages, food seasoning, aroma therapy, and traditional medicines since years ago. The local wisdom of Javanese people in Indonesia inherits knowledge from generation to other generations that ginger is one of the most important and efficacious herbal medicines for human's health [1].

Besides in Indonesia, utilization of ginger for traditional medicine has been well-known by people in other regions in the world. The Indian people have

utilized ginger for Ayurveda, the ancient medical system in India, since hundred years ago. In this case, ginger is one of the most important Ayurvedic herbs [2]. The Chinese people used ginger for anti-nausea, anti-vomiting [3], treatment for osteoarthritis [4], cancer preventive agent [5], and anti-radical activity [6]. Western medicine has utilized ginger for antimicrobial and antioxidant agents [7], medical treatment for a diabetic and hyperlipidaemia disease [8], and anti-cancer [9].

Ginger essential oil releases the specific odour and flavour that is distinguishable by human olfaction. The specific odour and flavour of ginger are generated by the combination of several major volatile compounds in ginger essential oil produced throughout the plant, especially at the rhizome. Different composition of major compounds generates different odour in ginger. Commonly, ginger odour exhibits a warm, sweet, bitter, and spicy taste with the slightly pungent mouth feel [10].

Ginger widely spread in some regions in the world, e.g.: Fiji, China, Brazil, and India. The largest ginger producing countries are mostly concentrated in Asia and Africa, i.e.: India, China, Nepal, Indonesia, Nigeria, and Thailand [11, 12]. Ginger has also many varieties, i.e.: Indian (Cochin, Calicut), Chinese, Jamaican, African, Hawaiian, Fijian, Nigerian, Japanese, Mexican, Australian, Thai and also Indonesian [13]. Commonly, the composition of the volatile compound in those gingers is nearly different depends on varieties and regions.

Indonesia has been one of ginger producer counties in the world. The total production of ginger from Indonesia is almost 0.233 million tons in 2013 [14]. Indonesian ginger has three varieties observed based on size and colour of rhizome, i.e.: small-white ginger (*Zingiber officinale var amarum*), big-white ginger (*Zingiber officinale var officinale*), and red ginger (*Zingiber officinale var rubrum*) [15]. In Indonesia, the utilization of these varieties of ginger is commonly different. The small-white ginger is usually used for Indonesian traditional herbal drink or *jamu gendhong,* while red ginger is usually used for medicinal purposes. The pharmaceutical industry in Indonesia has also utilized ginger as the raw material for producing herbal drink and herbal medicine [16]. The big-white ginger is usually used for spice, food flavouring, or traditional Javanese beverages (ginger drink or *wedang jahe* or *wedang ronde*). Due to different purposes, the composition of major compounds of these varieties of ginger may be different even the scent or odour is nearly similar.

In addition, the economic value of ginger depends on the taste, odour, flavour, and also the composition of bio-active compounds. The ginger that is rich in bio-active compounds e.g.: gingerol, α-zingibene, and 6-shogaol has high economic price due to efficacious for increasing human's health [17-21]. However, the volatile compounds, as well as the bio-active compounds identified in ginger essential oil are indistinguishable by human olfaction. The assessment of major volatile compounds in three varieties of Indonesian ginger (small-white ginger, big-white ginger, and red ginger) is necessarily carried out to increase the economic value of these Indonesian commodities.

Some previous research has been reported the identification of volatile organic compounds in ginger [22-26]. However, the previous articles that especially reported the identification of chemical constituents of Indonesian ginger using standard analytical instruments correlated with sensory analysis were still rare in International Journal. Some of them have been reported by [27-28]. Unfortunately, these papers did not describe specifically about the comparison of the chemical composition of volatile compounds among three varieties of herbals and the sensory response of them. Reference of [27] investigated the variation in the isozymic pattern of germplasm from three ginger varieties grown in Indonesia while [28] investigated simultaneous determination of gingerols and shogaol using capillary liquid chromatography and its application in discrimination of three ginger varieties from Indonesia.

Investigation of chemical compounds of three varieties of ginger grown in Indonesia correlated with sensory analysis using low-cost instrument is necessarily carried out. Based on previous references, the composition of chemical compounds in ginger essential oil was commonly identified using chromatographic techniques and non-chromatographic techniques. The most common chromatographic techniques for identification of volatile compounds in ginger used gas chromatography/ flame ionized detector (GC/FID) [26], gas chromatography/mass spectroscopy (GC/MS) [29], high-performance thin-layer chromatography (HPTLC) [30] and high-performance liquid chromatography (HPLC) [31].

Moreover, sensory analysis of ginger using electronic nose has been reported by [32-34]. Reference [32] analysed ginger flavour beverage by an electronic nose, partial least squares regression of descriptive sensory analysis and gas chromatography-mass spectrometry. Reference [33-34] reported employment of molecularly imprinted polymer-quartz crystal microbalance (MIP-QCM) for identifying bioactive compounds in ginger.

The aim of this study is to identify the major volatile compounds in three varieties of ginger grown in Indonesia using solid-phase micro extraction gas chromatography/mass spectroscopy (SPME-GC/MS) followed by sensory analysis. In the experiment, small-white ginger (*Zingiber officinale var. amarum*), big-white ginger (*Zingiber officinale var. officinale*), and red ginger (*Zingiber officinale var. rubrum*) were measured using SPME-GC/MS and e-nose based on metal oxide semiconductor gas sensor. Thus, the e-nose responses of these gingers were correlated to their volatile constituents.

2. Materials and Methods

2.1. Gingers

We used three varieties of ginger rhizome in this experiment. In April and May 2018, the rhizomes were collected from three different farms surrounding Banyumas Regency, Central Java Province, Indonesia during the harvesting period (see Table 1). These varieties of ginger rhizomes included: small-white ginger (*Zingiber officinale var. amarum*) or SWG, big-white ginger (*Zingiber officinale var. officinale*) or BWG, and red ginger (*Zingiber officinale var. rubrum*) or RG. For obtaining the optimum concentration of the volatile compound, we selected only fresh, wet and less than 3 days once harvesting process.

Table 1. List of location for obtaining sample of three varieties of ginger grown in Indonesia.

Variety	Location	Latitude Longitude	Altitude (m)
SWG	Sokawera village, surrounding Cilongok, Banyumas Regency, Central Java	N: -7.319938, E: 109.171692	658
BWG	Karanggondang, Sambirata village, surrounding Cilongok, Banyumas Regency, Central Java	N: -7.313662, E: 109.147474	580
RG	Gunung lurah village, surrounding Cilongok, Banyumas Regency, Central Java	N: -7.379301, E: 109.151232	410

2.2. Preparation of Sample

The sample preparation of ginger was very simple. Three varieties of Indonesian ginger collected from farms were washed using water to remove the soil which sticks to the skin of the rhizomes. Once the washing process, the ginger rhizomes were sliced. The dimension of the sliced sample is approximately 1 cm×1 cm×0.2 mm. Then, the slices of ginger were put in the different vial for SPME-GC/MS analysis.

2.3. SPME-GC/MS Instrument

The apparatus of SPME-GC/MS using Shimadzu GC/MS-QP-2010 (Kyoto, Japan), equipped with auto-sampler Agilent 7683b and MSD Agilent 5975C mass spectroscopy. GC/MS was coupled to QP 2010 SE mass spectrometer (Compaq-Pro Linear data system, class 5 K software). It was equipped with Agilent-DB-1 column (30 m×0.25 mm i.d. × 0.2 μm film thickness Crossband R 100 % dimethylpolysiloxane). A manual SPME holder, a type of fibre (65 μm-blue hub plain, polydimethylsiloxane/divinyl-benzene (PDMS/DVB)) and 10 mL vials from Supelco (Bellefonte, USA) were used for the extraction procedures.

2.4. SPME-GC/MS Analysis

A PDMS/DVB fibre was used for the extraction of the volatile organic compounds of three varieties of gingers. The fibres were conditioned for 10 min at 250 °C in the GC/MS injector before SPME-GC/MS analysis. For each variety of ginger sample, 1 g of sliced ginger rhizome was put in a 10-mL of the vial. The fibre coating was embedded into the headspace to determine temperature and time value set in the experiment. The temperature was set at 50 ºC while incubation and extraction time were set 5 min and 10 min, respectively. The fibre containing the extracted volatile compounds of ginger was injected into GC/MS injector. Direct injection of helium was used as carrier gas in the split mode. Injector and detector temperature were maintained at temperature 200-280 ºC. The measurement of each ginger sample using GC/MS equipped with auto-sampler was set for about 60 minutes. The temperature of the column was programmed initially at 70 ºC and then increased at 250 ºC for 10 minutes (at a rate of 18 °C min^{-1}). Mass conditions were followed: ionization voltage, 70 eV; ion source temperature, 200°C; full scan mode in the 30–450 amu mass ranges with 0.2 s scan-1 velocities. Identification of compounds was identified by using NIST 08 database (NIST mass spectral database, PC version 2008). The total ion current from GC/MS spectra was used to calculate the relative percentages of separated compounds by a computerized integrator.

2.5. Electronic Nose Apparatus

The e-nose used in this study was developed eight kinds of metal oxide semiconductor (MOS) sensors, i.e.: TGS 813, TGS 822, TGS 2600, TGS 826, TGS 2611, TGS 2620, TGS 2612, and TGS 2602 with dynamic headspace system (Fig. 1). The e-nose in this study has been used to investigate sensory response of 7 kinds of herbal medicines odour [35]. The block diagram of e-nose apparatus was presented in Fig. 2.

2.6. Data Recording

For data recording, a slice of ginger was put in sample handler heated at about 50 °C as the optimum temperature for releasing major volatile compounds. The control system of e-nose was set to be 1 minute for sensing process and 1 minute for flushing.

Fig. 1. The e-nose apparatus used to analyse sensory response of three varieties of gingers in this study.

In the sensing process, the control system set the F1 in ON condition (see Fig. 2). During the sensing process, gas molecules interacted with the metal oxide as the material of array gas sensor as a donor of charge carriers and decreased the resistivity of the metal oxide. Decreasing of resistivity of the metal oxide during the sensing process converted into a voltage signal. Oppositely, during the flushing process, the accumulation of gas molecules decreased gradually. Hence, the voltage signal decrease due to the increase of material sensor resistivity. The response of voltage signal of array gas sensor during sensing and flushing process is presented in Fig. 3. Totally, 150 slices of ginger rhizome including 50 slices of big white ginger, 50 slices of small white ginger, and 50 slices of red ginger were measured using e-nose.

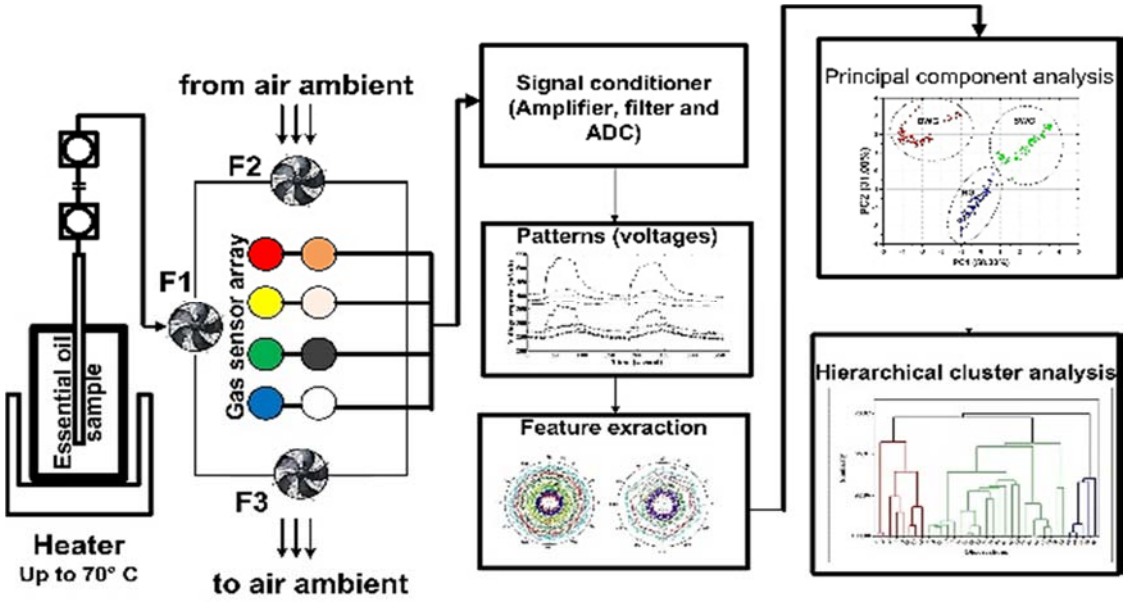


Fig. 2. Schematic block diagram of e-nose used in this study.

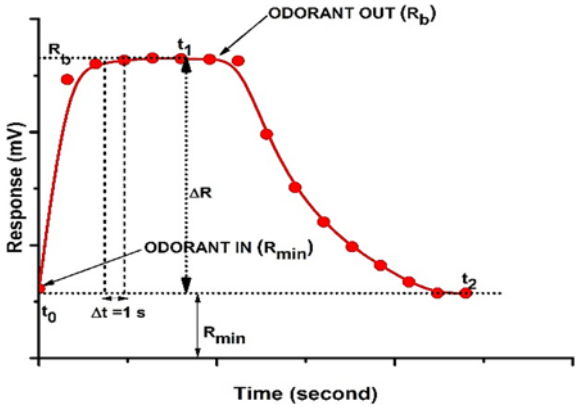


Fig. 3. The typical sensor response of a TGS gas sensor while measuring a ginger sample (one cycle consisted of sensing and flushing).

2.7. Feature Extraction

Data response of voltage signal obtained in the measurement of the ginger sample was extracted using a combination of relative amplitude (RA) and surface (SF) models (see eq. 1-eq. 2) [36].

Relative amplitude (RA)

$$RA = \frac{\Delta R}{R_b} = \frac{R_b - R_{min}}{R_b}, \quad (1)$$

where R_b and R_{min} are the sensor responses calculated at "Odorant in" and "Odorant out".

Surface (SF)

$$S = \sum_{t_1}^{t_2} R(t)\Delta t, \quad (2)$$

where $R(t)$ is the sensor response as time function, and Δt was calculated for 1 second.

Thus, the combination of relative amplitude and surface were normalized using $\boldsymbol{Z_{score}} = \frac{\boldsymbol{x-\mu}}{\boldsymbol{\sigma}}$, where $\boldsymbol{\mu}$ is the mean and $\boldsymbol{\sigma}$ is the standard deviation between relative amplitude and surface parameters.

3. Results and Discussion

3.1. Volatile Compounds in Three Gingers

Composition of major chemical compounds of three varieties of ginger investigated using SPME-GC/MS is presented in Table 2.

Table 2. List of major chemical compounds identified in three gingers using GC/MS analysis.

Compound name	Concentration (%)		
	SWG	BWG	RG
α-bisabolol	n/a	n/a	1.71
α-farnesene	14.01	n/a	n/a
(+)-epi-bicyclosesquiphel-landrene	n/a	0.91	n/a
2-undecanone	n/a	1.05	n/a
α-terpineol	3.88	2.17	2.94
α -zingiberene	n/a	33.44	13.99
β-bisabolene	n/a	16.03	n/a
β-elemene	2.03	0.84	n/a
β -eudesmol	1.91	n/a	1.21
β -farnesene	n/a	1.29	n/a
β-himachalene	3.73	1.30	n/a
β-sesquiphel-landrene	47.11	n/a	n/a
borneol	5.79	1.22	5.22
camphene	1.44	n/a	n/a
cedren-13-ol, 8-	n/a	23.78	n/a
citral	n/a	n/a	12.13
citronellol	n/a	1.23	3.54
curcumene	n/a	n/a	24.27
dehydronerolidol	1.72	n/a	1.71
elemol	n/a	n/a	1.18
eucalyptol	4.97	1.82	n/a
γ-muurolene	1.89	n/a	n/a
geraniol	n/a	n/a	9.99
geranyl acetate	n/a	n/a	1.19
globulol	2.40	n/a	n/a
ledene oxide-(I)	n/a	1.33	n/a
neral	5.10	11.90	17.32
nerol	n/a	n/a	2.04
nerolidol	3.01	1.69	1.50

SWG, the first variety of Indonesian ginger was dominated by β-sesquiphellandrene and α-farnesene. The abundances of these compounds in SWG were 47.11 % and 14.01 %, respectively (Table 2). Other major compounds identified in SWG were: borneol (5.79 %), neral (5.10 %), eucalyptol (4.97 %), α-terpineol (3.88 %), β-himachalene (3.73 %), nerolidol (3.01 %), globulol (2.40 %), β-elemene (2.03 %), β-eudesmol (1.91 %), γ-muurolene (1.89 %), dehydronerolidol (1.72 %) and camphene (1.44 %). β-sesquiphellandrene, the largest compound identified in SWG is a member of the class of compounds known as sesquiterpenoids, the terpenes with three consecutive isoprene units. This compound is efficacious for the human such as antimicrobial, antioxidant, anti-tumour and anti-cancer [37-38]. Furthermore, α-farnesene, a sesquiterpene, was the second largest chemical compound identified in SWG. The α-farnesene has green apple odour [39]. Based on the previous report, this compound was efficacious for teeth decay prevention (anti-cariogenic) and anti-microbial agent [40-41]. In addition, other chemical compounds identified in lower abundance in SWG were borneol and neral. Borneol is a bicyclic organic compound and a terpene derivative, had camphor-like odour and burning taste somewhat reminiscent of mint, while neral has a spicy, fruit odour with a woody, balsamic undernote and a sweet, warm, powerful, and spicy taste [39]. Borneol was efficacious as anti-influenza virus and anti-depressant. [42-43].

BWG was the second variety of ginger identified using SPME-GC/MS. From Table 2, it can be shown that the major chemical compounds of BWG were dominated by: α-zingiberene (33.44 %), cedren-13-ol, 8- (23.78 %), β-bisabolene (16.03 %) and neral (11.90 %). The α-zingiberene, the largest quantity identified in BWG is a monocyclic sesquiterpene that is a commonly predominant constituent of the essential oil of many varieties of ginger. This compound has a warm, woody-spicy and very tenacious odour [39]. The α-zingiberene has been reported as a bio-active compound that is efficacious for antioxidant [44]. β-bisabolene, a sesquiterpene, exhibited cytotoxicity in breast cancer cell lines, and anti-tumour agent [45]. Furthermore, neral, a mono terpenoid aldehyde, has been widely used as a powerful lemon-fragrance chemical [39]. In previous research, this compound has anti-inflammatory activity [46].

Chemical composition identified in RG were dominated by: curcumene (24.27 %), neral (17.32 %), α-zingiberene (13.99 %), citral (12.13 %), geraniol (9.99 %), borneol (5.2 %), citronellol (3.54 %), α-terpineol (2.94 %), nerol (2.04 %), α-bisabolol (1.71 %), dehydronerolidol (1.71 %), nerolidol (1.50 %), β-eudesmol (1.21 %), geranyl acetate (1.19 %), and elemol (1.18 %). Citral and neral are isomers. Hence, these compounds were considered equal and are counted as the largest constituent of RG. Totally, the abundance of these two compounds was 29.45 %. The odour and the taste of citral was almost similar to neral, had a spicy, fruit odour with a woody, balsamic undernote and a sweet, warm, powerful, spicy taste [38]. Previous research investigated that citral was also efficacious as antifungal, antimicrobial, antioxidant, and anti-tumour activity [47-48]. Curcumene, the major compound commonly found in turmeric, was identified 24.27 % in RG. This compound showed slightly pungent bitter taste [39]. Curcumene showed effective properties for anti-

inflammatory, anti-bio insecticide and anti-toxic for malaria, and chikungunya disease [49]. The other volatile compound identified was geraniol. Even it was only identified 9.99 %, this compound has been investigated as a bio-active compound that was efficacious for anti-inflammatory, cancer chemotherapy, cytotoxicity against fibrosarcoma, anti-bacterial agent, and anti-Parkinson disease [50-53].

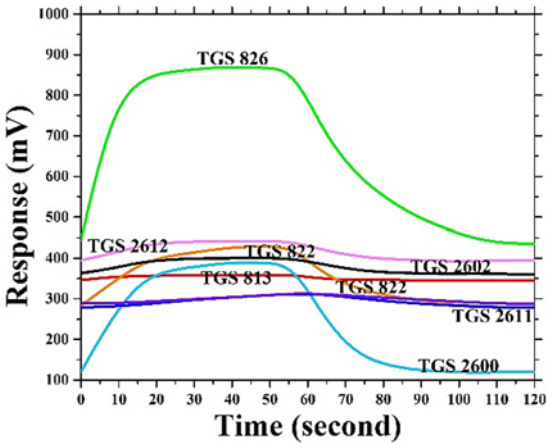
The composition of major compounds in Table 2 can be used to predict the similarity of aroma among three gingers. SWG was dominated β-sesquiphellandrene and α-farnesene. The major chemical compound identified in SWG were: α-zingiberene, cedren-13-ol, 8-, β-bisabolene, and neral (11.90 %). Meanwhile, curcumene, neral, α-zingiberene, citral, and geraniol were most dominant in RG. Based on composition of major compound in these gingers, the aroma of BWG was most similar to RG than SWG due to presence of α-zingiberene and neral more than 10 % both in BWG and RG. Sensory analysis using e-nose based on MOS gas sensor was used to verify the similarity of aroma among three gingers.

3.2. E-nose Response of Three Gingers

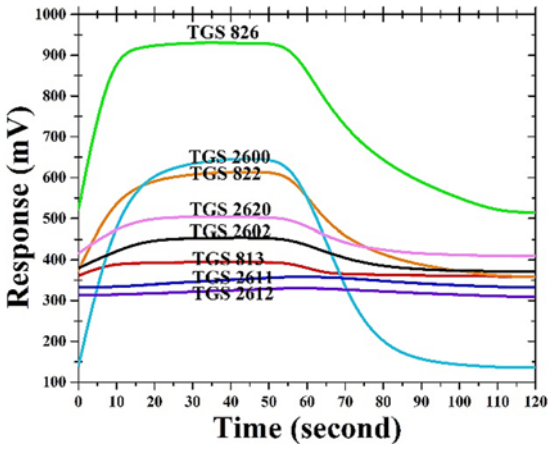
The typical e-nose responses of ginger including SWG, BWG and RG without feature extraction are presented in Fig. 4. Fig. 4(a) visualizes the response of e-nose obtained by measuring a sample of SWG. The e-nose response contains parameters which consists of baseline value, the amplitude of signal, and the area under the curve of response. Each sensor has different value for these parameters due to different sensitivity and selectivity toward gas molecule released by SWG essential oil.

Furthermore, the difference of e-nose response among three varieties of ginger, i.e.: SWG, BWG, and RG can be distinguished by observing feature extraction of eight sensor responses based on relative RA and SF (see Fig. 4(a), Fig.4(b), and Fig. 4(c)). The RA counted the amplitude of sensor response divided by baseline value, while the SF calculated the area under the curve of e-nose response. Parameters of RA and SF then was used to extract the features of e-nose response. The values of RA and SF then normalized using z-score for further analyses using principal component analysis and hierarchical cluster analysis.

Table 3 shows the feature response of gingers using RA and SF parameters without z-score normalization. The values of RA and SF in Table 3 corresponds to the sensitivity of each TGS sensor toward gas molecules of gingers. The TGS sensors which was higher sensitive toward gas molecules of gingers had high RA and SF values. Oppositely, the TGS sensors with lower RA value showed lower sensitivity among the gas molecules of three gingers. For the threshold values, we took the value of RA was more than 0.10 and SF was more than 3000. The RA and SF values which exceeded threshold were shown by 4 sensors, i.e. TGS 822, TGS 2600, TGS 826, and TGS 2620. These sensors indicated highly sensitive and selective toward gas molecule of gingers. Meanwhile, other sensors, including TGS 813, TGS 2611, TGS 2620 and TGS 2612 showed not sensitive and selective towards gas molecules of gingers.



(a)



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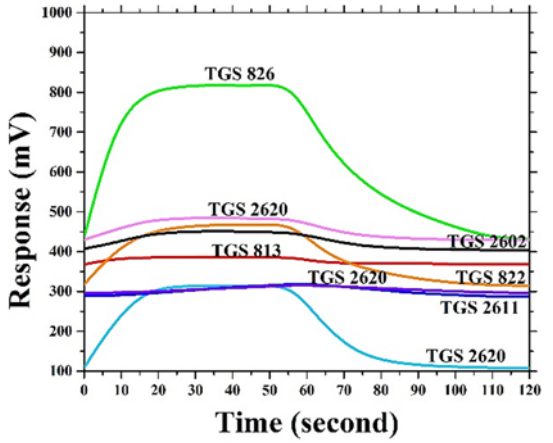

(c)

Fig. 4. Typical e-nose response of gingers without feature extraction: small-white ginger (SWG); (b) big-white ginger (BWG); and (c) red ginger (RG).

Table 3. The values of feature response of three samples of ginger including SWG, BWG, and RG extracted using RA and SF as feature extraction techniques without z-score normalization.

Parameter	Sensor	Feature value		
		SWG	BWG	RG
RA	TGS 813	0.05	0.09	0.04
	TGS 822	0.33	0.42	0.35
	TGS 2600	0.66	0.79	0.70
	TGS 826	0.47	0.45	0.50
	TGS 2611	0.10	0.07	0.11
	TGS 2620	0.12	0.19	0.11
	TGS 2612	0.06	0.06	0.08
	TGS 2601	0.10	0.18	0.10
SF	TGS 813	5655	5483	5784
	TGS 822	5904	8077	7541
	TGS 2600	3149	5818	4380
	TGS 826	9718	11167	11320
	TGS 2611	4520	5337	4600
	TGS 2620	6841	6813	7762
	TGS 2612	4574	5133	4726
	TGS 2601	6402	6034	7483

In addition, the performance of array sensor for discriminating of three gingers was analysed using multivariate techniques based on principal component analysis (PCA) and hierarchical cluster analysis (HCA). Principal component analysis (PCA) is one of pattern recognition techniques used to analyse of target vapour using e-nose. The PCA is a statistical technique used to simplify the dimensionality of numerical data sets and convert a set of observations of correlated variables into a set of values of uncorrelated variables called as principal components. Since patterns of data are difficult to find in high dimension, PCA was used to reduce the number of data dimensions without much loss of information. In this case, PCA is applied to reduce the data dimension of feature of sensor response obtained from the eight MOS sensor array. In this case, the datasets were obtained by measuring 150 slices of gingers using 8 MOS sensor. All responses then were extracted using RA and SF parameters. PCA converted datasets into 2 principal components with highest eigen values and also reduced dimension of feature e-nose response from 16×150 to 2×150.

Fig. 5 presents the score plot in the PC_1-PC_2 coordinate of three different clusters of three gingers. In total, 97.10 % of variance has been retained from four principal components. PC_1 contributed 58.30 % of variance, while PC_2 contributed 31.00 %. Meanwhile, the variance contribution of PC_3 and PC_4 were 5.20 % and 2.60 % respectively. Hence, only first two of principal components that significantly contributed the variance of PCA score plot.

Furthermore, hierarchical cluster analysis (HCA) was used to analyse the similarity pattern of the feature e-nose response among three gingers. In principal, the HCA is a statistical method used to divide a group of objects into several clusters based on the similarity of the object. Hence, the similar objects are put in the same clusters. Oppositely, different objects are put in different clusters. In this study, HCA was used to measure similarity level of feature response among 3 kinds of ginger. Fig. 6 and Fig. 7 present the dendrogram of HCA analysis to visualize the similarity level of 60 response of three gingers into two and three different clusters.

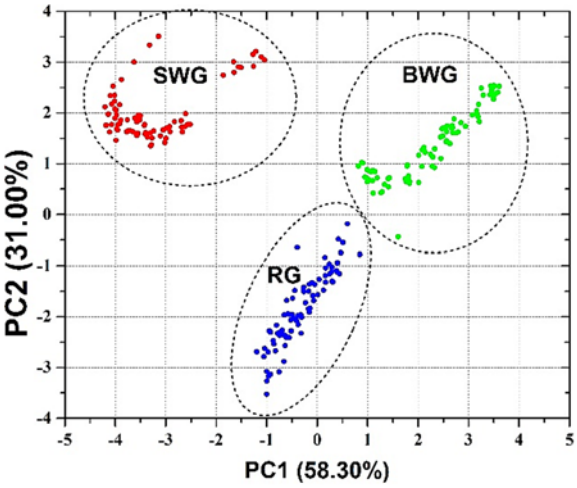

Fig. 5. PCA score plot of 150 feature responses of three gingers in 2 principal components coordinate.

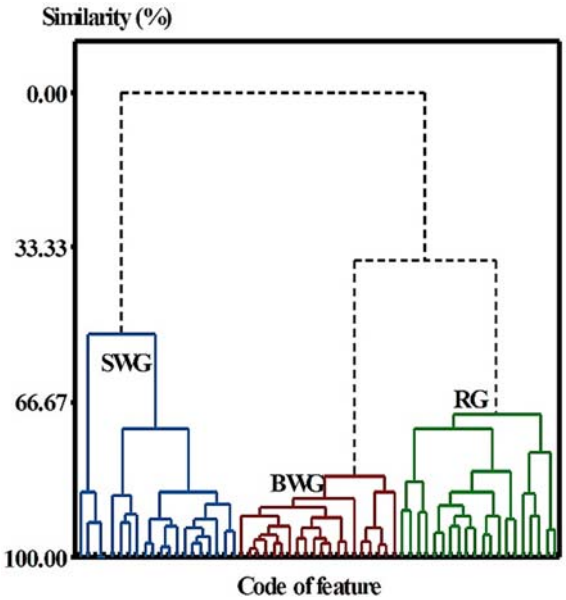

Fig. 6. Dendrogram visualization for clustering 60 response of three gingers into three clusters.

Clustering of 60 feature response into 3 groups obtained 52.16 % of similarity level for 20 feature responses of SWG, while 20 feature responses of BWG and 20 feature responses RG reach 82.62 % and 69.31 % of similarity level, respectively (see Fig. 6).

While 60 feature responses were grouped only into 2 clusters, feature of BWG is most similar to RG than SWG. The similarity level between SWG and RG is almost 36.12 %, while similarity level between SWG and BWG, as well as SWG and RG are 0 %. Similarity of feature response between BWG and RG was contributed by similarity of major compounds in BWG and RG.

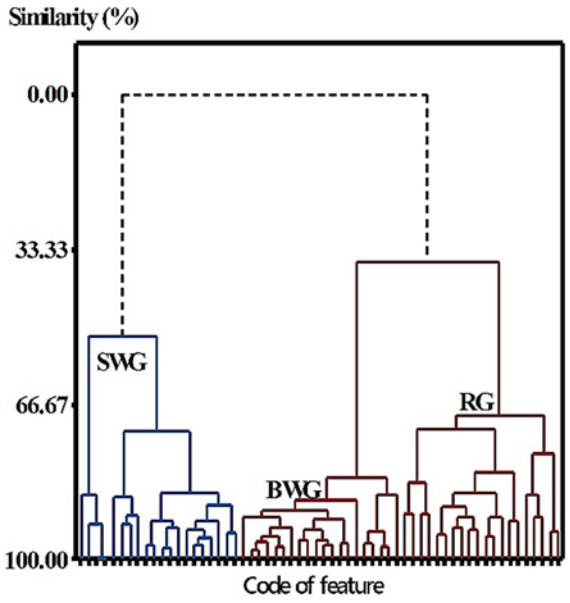

Fig. 7. Dendrogram visualization for clustering 60 response of three gingers into two clusters that estimates similarity level of e-nose response among three gingers.

4. Conclusions

SPME-GC/MS analysis followed by sensory analysis using electronic nose has been employed to investigate major volatile compounds and aroma in three varieties of gingers. SPME GC/MS identified twenty-nine major chemical compounds in three gingers. SWG, the first variety of Indonesia ginger was dominated by β-sesquiphellandrene and α-farnesene. BWG, the second variety of Indonesian ginger was dominated by: α-zingiberene, cedren-13-ol, 8-, β-bisabolene, and neral, while RG was dominated by citral, curcumene, α-zingiberene, and geraniol. Based on composition of major compounds, the aroma of BWG most similar to RG than SWG due to presence of α-zingiberene and neral both in BWG and RG. Sensory analysis using e-nose was able to discriminate the aroma in three gingers. Analyses of feature e-nose response based on PCA and HCA show that the aroma of three gingers can be distinguished by e-nose. The score plot of PCA contributes 89.30 % in two principal coordinates. Meanwhile, dendrogram of HCA shows the similarity between BG and RG for about 36.12 %. Employment of low-cost e-nose instrument based on eight MOS gas sensor shows good performance for rapid discrimination in three varieties of ginger with simple preparation and high repeatability.

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References

[1]. M. T. Al Makmun, S. E. Widodo, Sunarto, Construing traditional Javanese herbal medicine of headache: Transliterating, translating, and interpreting Serat Primbon Jampi Jawi, *Procedia Social and Behavioral Sciences*, Vol. 134, 2014, pp. 238-245.

[2]. S. S. Tirtha, The ayurveda encyclopedia, Natural secrets to healing, prevention & longevity, *Ayurveda Holistic Center Press*, New York, 1998.

[3]. E. Soltani, A. Jangjoo, A. M. Aghaei, A. Dalili, Effects of preoperative administration of ginger (*Zingiber officinale Roscoe*) on postoperative nausea and vomiting after laparoscopic cholecystectomy, *Journal of Traditional and Complementary Medicine,* Vol. 8, Issue 3, 2017, pp. 387-390.

[4]. B. D. Alper, M. Molone-Moses, E. W. Manheimer, Evidence for clinical practice point-of-care application of: 'Efficacy and safety of ginger in osteoarthritis patients: A meta-analysis of randomized placebo-controlled trials', *European Journal of Integrative Medicine,* Vol. 8, Issue 5, 2016, pp. 621-622.

[5]. Y. Shukla, M. Singh, Cancer preventive properties of ginger: A brief review, *Food and Chemical Toxicology*, Vol. 45, Issue 5, 2007, pp. 683-690.

[6]. E. S. Alinkina, T. A. Misharina, L. D. Fatkullina, E. B. Burlakova, Comparison of the antiradical activity of ionol, components of fresh ginger, and its extracts, *Applied Biochemistry and Microbiology*, Vol. 48, Issue 5, 2012 pp. 513–518.

[7]. S. Noori, F. Zeynali, H. Almasi, Antimicrobial and antioxidant efficiency of nanoemulsion-based edible coating containing ginger (*Zingiber officinale*) essential oil and its effect on safety and quality attributes of chicken breast fillet, *Food Control*, Vol. 84, 2018, pp. 312-320.

[8]. S. Jafarnejad, S. A. Keshavarz, S. Mahbudi, S. Saremi A. Arab, S. Abbasi, K. Djafarian, Effect of ginger (*Zingiber officinale*) on blood glucose and lipid concentrations in diabetic and hyperlipidemic subjects: A meta-analysis of randomized controlled trials, *Journal of Functional Foods*, Vol. 29, 2017, pp. 127-134.

[9]. W. N. N. Nabil, R. J. Lim, S. Y. Chan, N. M. Lai, A. C. Liew, A systematic review on Chinese herbal treatment for radiotherapy-induced xerostomia in head and neck cancer patients, *Complementary Therapies in Clinical Practice*, Vol. 30, 2018, pp. 6-13.

[10]. S. Arctander, Perfume and flavor chemicals (Aroma chemicals), *Montclair*, New York, 1969.

[11]. J. A. Duke, M. J. Bogenschutz-Godwin, J. duCellier, CRC Handbook of Medicinal Spices, *CRC Press*, London, 2003.
[12]. P. N., Ravindran, K. N. Babu, Ginger the Genus Zingiber, Medicinal and Aromatic Plant-Industrial Profiles, *CRC Press,* New York, 2005.
[13]. S. Raghavan, Handbook of spices, seasoning, and flavorings, 2nd edition, *CRC Press*, London, 2007.
[14]. K. V. Peter, Handbook of Herbs and Spices, *CRC Press*, 2004.
[15]. J. J. Ochse, R. C. Bakhuisen van den Brink, Vegetables of the Dutch East Indies, *Archipel Drukkerij,* Buitenzorg, 1931.
[16]. Elfahmi H. J. Woerdenbag, O. Kayser, Jamu: Indonesian traditional herbal medicine towards rational phytopharmacological use, *Journal of Herbal Medicine,* Vol. 4, Issue 2, 2014, pp. 51-73.
[17]. M. M. Bernard, J. R. McConnery, D. W. Hoskin, [10]-gingerol, a major phenolic constituent of ginger root, induces cell cycle arrest and apoptosis in triple-negative breast cancer cells, *Experimental and Molecular Pathology,* Vol. 102, Issue 2, 2017, pp. 370-376.
[18]. R. B. Semwal, D. K. Semwal, S. Combrinck, A. M. Viljoen, Gingerols and shogaols: Important nutraceutical principles from ginger, *Phytochemistry*, Vol. 117, 2015, pp. 554-568.
[19]. W. Si, Y. P. Chen, J. Zhang, Z.-Y. Chen, H. Y. Chung, Antioxidant activities of ginger extract and its constituents toward lipids, *Food Chemistry*, Vol. 239, 2018, pp. 1117-1125.
[20]. K. Srinivasan, Ginger rhizomes (Zingiber officinale): A spice with multiple health beneficial potentials, *Pharma Nutrition*, Vol. 5, Issue 1, 2017, pp. 18-28.
[21]. K. An, D. Zhao, Z. Wang, J. Wu, Y. Xu, G. Xiao, Comparison of different drying methods on Chinese ginger (*Zingiber officinale Roscoe*): Changes in volatiles, chemical profile, antioxidant properties, and microstructure, *Food Chemistry*, Vol. 197, Part B, 2016, pp. 1292-1300.
[22]. S. H. Ding, K. J. An, C. P. Zhao, Y. Li, Y. H. Guo, Z. F. Wang, Effect of drying methods on volatiles of Chinese ginger (*Zingiber officinale Roscoe*), *Food and Bioproducts Processing*, Vol. 90, Issue 3, 2012, pp. 515-524.
[23]. A. Jelled, A. Fernandes, L. Barros, H. Chahdoura, L. Achour, I. C. F. R. Ferreira, H. B. Cheikh, Chemical and antioxidant parameters of dried forms of ginger rhizomes, *Industrial Crops and Products,* Vol. 77, 2015, pp. 30-35.
[24]. M. C. Mesomo, M. L. Corazza, P. M. Ndiaye, O. R. D. Santa, L. Cordozo, A. P. Scheer, Supercritical CO_2 extracts and essential oil of ginger (*Zingiber officinale R.*): Chemical composition and antibacterial activity, *The Journal of Supercritical Fluids*, Vol. 80, 2013, pp. 44-49.
[25]. M. Rafi, L. W. Lim, T. Takeuchi, L. K. Darusman, Simultaneous determination of gingerols and shogaol using capillary liquid chromatography and its application in discrimination of three ginger varieties from Indonesia, *Talanta*, Vol. 103, 2013, pp. 28-32.
[26]. A. Toure, Z. Xiaomin, Gas chromatographic analysis of volatile components of Guinean and Chinese ginger oils (*Zingiber officinale*) extracted by steam distillation, *J. Agron*, Vol. 6, Issue 2, 2007, pp. 350-355.
[27]. A. D. Setyawan, Wiryanto, Suranto, N. Bermawi, Short Communication: Variation in isozymic pattern of germplasm from three ginger (*Zingiber officinale*) varieties, *Nusantara Bioscience,* Vol. 6, Issue 1, 2014, pp. 86-93.
[28]. M. Rafi, L.W. Lim, T. Takeuchi, L. K. Darusman, Simultaneous determination of gingerols and shogaol using capillary liquid chromatography and its application in discrimination of three ginger varieties from Indonesia, *Talanta*, Vol. 103, 2013, pp. 28-32.
[29]. G. B. Barbarosa, N. S. Jayasinghe, S. H. A. Natera, E. D. Inutan, N. P. Peteros, U. Roessner, From common to rare Zingiberaceae plants - A metabolomics study using GC-MS, *Phytochemistry*, Vol. 140, 2017, pp. 141-150.
[30]. S. Kruger, A. Bergin, G. E. Morlock, Effect-directed analysis of ginger (*Zingiber officinale*) and its food products, and quantification of bioactive compounds via high-performance thin-layer chromatography and mass spectrometry, *Food Chemistry*, Vol. 243, 2018, pp. 258-268.
[31]. S. Saha, R. M. Smith, E. Lenz, I. D. Wilson, Analysis of a ginger extract by high-performance liquid chromatography coupled to nuclear magnetic resonance spectroscopy using superheated deuterium oxide as the mobile phase, *Journal of Chromatography A*, Vol. 991, Issue 1, 2003, pp. 143–150.
[32]. F. Liu, S. Song, X. Zhang, C. Tan, E. Karangwa, Effect of sterilization methods on ginger flavor beverage assessed by partial least squares regression of descriptive sensory analysis and gas chromatography–mass spectrometry, *European Food Research and Technology,* Vol. 228, Issue 2, 2014, pp. 247-257.
[33]. J. Cao, S. Zhou., W. Kong, M. Yang, L. Wan, S. Yang, Molecularly imprinted polymer-based solid phase clean-up for analysis of ochratoxin in ginger and LC-MS/MS confirmation, *Food Control,* Vol. 33, Issue 2, 2013, pp. 337-343.
[34]. W. Ji, X. Ma, J. Zhang, H. Xie, F. Liu, X. Wang, Preparation of the high purity gingerols from ginger by dummy molecularly imprinted polymers, *Journal of Chromatography A*, Vol. 1387, 2015, pp. 24–31.
[35]. F. Hardoyono, K. Triyana, K., B. H. Iswanto, Rapid Discrimination of Indonesian Herbal Medicines by Using Electronic Nose Based on Array of Commercial Gas Sensors, *Applied Mechanics and Materials*, Vol. 771, 2015, pp. 209–212.
[36]. K. Brudzewski, J. Ulaczy, An effective method for analysis of dynamic electronic nose responses, *Sensors and Actuators B*, Vol 140, Issue 1, 2009, pp. 43–50.
[37]. E. V. Costa, L. R. A. Menezes, S. L. A. Rocha, I. R. S. Baliza, R. B. Dias, C. A. G. Rocha, M. B. P. Soares, D. P. Bezerra, Antitumor Properties of the leaf essential oil of Zornia brasiliensis, *Planta Medica,* Vol. 81, Issue 7, 2015, pp. 563-567.
[38]. A. K. Tyagi, S. Prasad, W. Yuan, S. Li, B. B. Aggarwal, Identification of a novel compound (β-sesquiphellandrene) from turmeric (*Curcuma longa*) with anticancer potential: comparison with curcumin, *Investigational New Drugs*, Vol. 33, Issue 6, 2015, pp. 1175-1186.
[39]. G. Burdock, Fenaroli's Handbook of Flavor Ingredients, 6th ed., *CRC Press*, New York, 2010.
[40]. K. B. Ishnava, J. B. Chauhan, M. B. Barad, Anticariogenic and phytochemical evaluation of Eucalyptus globules labill, *Saudi Journal of Biological Sciences*, Vol. 20, Issue 1, 2013, pp. 69-74.
[41]. F. Maggi, C. Cecchilini, A. Cresci, M. M. Coman, B. Tirillini, G. Sagratini, F. Papa, Chemical composition and antimicrobial activity of the essential oil from

Ferula glauca L. (F. *communis* L. subsp. *glauca*) growing in Marche, *Fitoterapia*, Vol. 80, Issue 1, 2009, pp. 68-72.
[42]. A. S. Sokolova, O. I. Yarofaya, M. D. Semenova, A. A. Shtro, R. Orshanskaya, V. V. Zarubaev, N. F. Salakhudinov, Synthesis and in vitro study of novel borneol derivatives as potent inhibitors of the influenza A virus, *Medical Chemical Communication,* Vol. 8, Issue 5, 2017, pp. 960-963.
[43]. T. Huo, X. Li, C. Peng, Borneol enhances the antidepressant effects of asiaticoside by promoting its distribution into the brain, *Neuroscience Letters*, Vol. 646, 2017, pp. 56-61.
[44]. H.-Y. Yeh, C.-H. Chuang, H.-C. Chen, C.-J. Wan, T.-L. Chen, L.-Y. Lin, Bioactive components analysis of two various gingers (*Zingiber officinale Roscoe*) and antioxidant effect of ginger extracts, *LWT - Food Science and Technology*, Vol, 55, Issue 1, 2014, pp. 329-334.
[45]. S. K. Yeo, A. Y. Ali, O. A. Hayward, D. Turnham, T. Jackson, I. D. Bowen, R. Clarkson, β-bisabolene, a sesquiterpene from the essential oil extract of opoponax (*Commiphora guidottii*), exhibits cytotoxicity in breast cancer cell lines, *Phytotheraphy Research*, Vol. 30, Issue 3, 2016, pp. 418-425.
[46]. P.-C. Liao, T.-S. Yang, J.-C. Chou, J. Chen, S.-C. Lee, Y.-H. Kuo, C.-L. Ho, L. K.-P. Chao, Anti-inflammatory activity of neral and geranial isolated from fruits of Litsea cubeba Lour, *Journal of Functional Foods*, Vol. 19, Part A, 2005, pp. 248-258.
[47]. M. C. A. Leite, A. P. B. Berezza, J. P. de Sousa, F. Q. Queiroga, S. Guerra, E. O. Lima, Evaluation of antifungal activity and mechanism of action of citral against *Candida albicans*, *Evidence-based Complementary & Alternative Medicine,* Vol. 2014, 2014, pp. 1-9.
[48]. C. Shi, X. Zhao, Z. Liu, R. Meng, X. Chen, N. Guo, Antimicrobial, antioxidant, and antitumor activity of epsilon-poly-L-lysine and citral, alone or in combination, *Food & Nutrition Research*, Vol. 60, Issue 1, 2016, pp. 1-8.
[49]. M. M. AlShelby. F. S. AlQahtani, M. Govindarajan, K. Gopinanth, P. Vijayan, G. Benelli, Toxicity of ar-curcumene and epi-β-bisabolol from *hedychiumlarsenii* (Zingiberaceae) essential oil on malaria, chikungunya and St. Louis encephalitis mosquito vectors, *Ecotoxicology and Environmental Safety*, Vol. 137, 2017, pp. 149-157.
[50]. M. Galle, R. Crespo, K. Rodenak, R. K. Boris, S. M. Villegas, P. Mónica, M. G. de Bravo, Suppression by geraniol of the growth of A549 human lung adenocarcinoma cells and inhibition of the mevalonate pathway in culture and in vivo: potential use in cancer chemotherapy, *Nutrition & Cancer,* Vol. 66, Issue 5, 2014, pp. 888-895.
[51]. M. Safaepour, A. R. Shahverdi, H. R. Shahverdi, M. R. Khorramizadeh, A. R. Gohari, Green synthesis of small silver nanoparticles using geraniol and its cytotoxicity against Fibrosarcoma-Wehi 164, *Avicenna Journal of Medical Biotechnology*, Vol. 1, Issue 2, 2009, pp. 111-115.
[52]. L. Yue, J. Li, W. Chen, X. Liu, Q. Jiang, W. Xia, Geraniol grafted chitosan oligosaccharide as a potential antibacterial agent, *Carbohydrate Polymer*, Vol. 176, 2017, pp. 356-364.
[53]. Y. H. Siddique, F. Naz, S. Jyoti, F. Ali, A. Fatima, Rahul, S. Khanam, Protective effect of geraniol on the transgenic Drosophila model of Parkinson's disease, *Environmental Toxicology and Pharmacology*, Vol. 43, 2016, pp. 225-231.