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Research Article

Fruit Volatile Fingerprints Characterized among Four Commercial Cultivars of Thai Durian (*Durio zibethinus*)

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Ripe durian fruits produce unique volatiles of pungent odor comprising esters, alcohols, ketones, and sulfur-containing compounds. Recently, "Chanthaburi 1" hybrid bred from 2 famous commercial cultivars of "Chanee" and "Monthong" claimed to be less fragrant during ripening, but there was no report. The present study compared the volatile profiles from 3 Thai commercial cultivars of "Kanyao," "Chanee," and "Monthong" compared to "Chanthaburi 1", and the relationships of the cultivars were organized using the volatile fingerprints. Out of 41 volatile compounds detected by SPME/GC-MS in ripe durian flesh, 33 compounds were esters, but only 14 esters were found in "Chanthaburi 1." Ripe flesh of most durian cultivars contains ethyl-2-methyl butanoate and ethyl hexanoate as the active volatiles. "Chanthaburi 1" contained fewer components with low odor activity value (OAV) of the volatiles. "Chanee" ripe flesh exhibited the strongest durian smell among the four varieties, whereas "Monthong" exhibited a strong apple-like fruity odor and "Kanyao" was more green fruity. Diethyl disulfide and 3, 5 dimethyl-1, 2, 4-trithiolane contributing pungent smells of garlic or onion were found only in "Chanthaburi 1" and "Monthong." In terms of detected volatiles, "Kanyao" and "Chanee" were highly close when "Monthong" was apart. PCA analysis revealed that "Chanthaburi 1" contained ester compounds ancestrally related to the parents, "Chanee" in the component I and "Monthong" in the component II. These data could be beneficial for managing the status of Thai durians in global markets.

1. Introduction

In Thailand, durian plant collection was firstly reported for 227 varieties. However, there currently are several cultivars, including "Chanee," "Kanyao," and "Monthong," in the business both in domestic and export markets [1]. "Chanee" comprises a moderate fruit size of 2.5–3 kg. The fruit shape shows swelling in the middle and is blunt at the blossom end with a big and short peduncle. When ripening, fruit is easily peeled, and the yellow flesh is a very soft fine texture, but with the thin flesh and an ample seed, it is famous for domestic markets. "Kanyao" bears a moderate fruit size of 3 kg, showing a round fruit shape and a big and long peduncle. The ripe flesh has smoothly fine texture and is yellow and sweet. "Monthong," the most famous variety, exhibits big fruit of 3–4 kg. Fruit is long, having shoulders at the stem end and protruding at the blossom end. The ripe flesh is dry and thick with a lean seed [2–4]. Ripe fruits of most typical durian varieties release a pungent solid smell, resulting in trouble for foreigners and under public assemblage. Recently, "Chanthaburi 1" (ICN $\times$ *M* 5-1-1), bred from "Chanee" and "Monthong," was officially approved and registered as a new variety by the Department of Agriculture, Thailand, on 9 October 2006. The fruit is an early-season production with a harvesting time of 99–105 days after pollination. The average fruit weight is 2.5–3 kg, comprising bright yellow flesh and a sweet, delicate texture. The ripe fruit of "Chanthaburi 1" is claimed to have an extra-low smell [5]. Nevertheless, there is no analytical report yet for the volatile characterization of the fruit.

Aroma is a unique character of ripe durian fruit preferred by some but annoying for many people. Furthermore, it is seriously prohibited to take durian fruit/eat during public transportation or in assembly places such as hotels or convention halls. This matter would be a significant obstacle for the marketing of durians. Ethyl esters (fruity esters and general fruit) are the prominent esters in ripe "Monthong" flesh [6, 7]. Nevertheless, this sweet smell is interrupted by sulfurous smells of sulfur-containing compounds. Ethanethiol, diethyltrisulfide, diethyldisulfide, dimethyl sulfide, 2,3-butanedithiol, ethyl 1-methylethyl disulfide, 3-methyl-thiozolidine, methyl ethyl disulfide, and 1-propanethiol are such sulfur-containing compounds found in ripe durian flesh [6–8]. There is no report of the relationship of durian cultivars by the aroma volatile so far. There have been many reports of volatile components of ripe durians in "Monthong" [6–9], few in "Chanee" [6], but there is no report in "Kanyao" and "Chanthaburi 1." Furthermore, from the fruit's visual appearance, "Chanthaburi 1" fruit shape is very similar to the shape of "Kanyao," leading to confusion by visual appearance. Thus, fruit volatile profiles between the cultivars compared as volatile fingerprints were brought in the interest. Here, the present study was to identify odor characteristics of 4 commercial varieties. Volatiles of "Kanyao" and "Chanthaburi 1" were firstly reported, and the volatile relationship of these four varieties was then investigated.

2. Materials and Methods

2.1. Plant Materials and Sample Preparation. Mature durian fruits at 90% maturation from 4 cultivars, "Chanee" (1.9–2.2 kg) at 15 weeks after anthesis (WAA), "Kanyao" at 18 WAA (1.7–2.0 kg), "Monthong" at 19 WAA (2.2–2.8 kg), and 'Chanthaburi 1 at 14 WAA (1.4–1.8 kg), were harvested from commercial orchards in Chanthaburi Province, eastern Thailand, between April and June 2018. Fruits were incubated at room temperature (25°C, 70–75% RH) for natural ripening. Fruit showing initial dehiscence at the blossom end (Supplementary Figure 1), referred to as full ripening, was peeled, and the ripe flesh was used for volatile analysis. The visual appearance of the whole fruit and half-dehusked of ripe fruits of the four cultivars is shown in Figure 1.

2.2. Chemicals. The internal standard of volatile analysis was thiophene (≥99% purity) (Sigma Chemical Co., USA).

2.3. Volatile Trapping. The ripe aril of each cultivar was finely blended by using a high-speed homogenizer for 2 min. Homogenate at 5 g was put into a 20 mL glass vial sealed with a screw cap having a silicone laminated with polytetrafluoroethylene septum. The volatiles in the sample's headspace were trapped by SPME and analyzed by GC-MS modified from [10]. The volatiles in the headspace of the sample in a vial were trapped by solid-phase microextraction (SPME) coated with 65 μm of Polydimethylsiloxane/Divinylbenzene (PDMS/DVB) (1 cm length), while heated at 50°C for 30 min.

2.4. Analysis of Volatiles in Ripe Durian Flesh. The SPME was injected into a gas chromatogram (GC 6850 series, Agilent Technologies, USA), equipped with an HP-5MS column (5% phenyl-methylsiloane capillary column, 30m × 0.248 mm I.D. with 0.25 μm thickness) and an Agilent 5913 mass selective detector with the following condition: 200°C of the injection port (splitless mode), 50°C of the column oven for 1 min and increased at a rate of 5°C·min^{-1} to 120°C and then to 250°C at a 10°C·min^{-1} rate, and 250°C of the detector. Helium was the carrier gas set to 2 mL·min^{-1} at 15.9 psi.

Thiophene at 10 μL·L^{-1} was used as the internal standard. The spectra of the volatile profile were analyzed in the electron impact (EI) mode with an electron energy of 70 eV; a mass range of m/z 45–450; a scan rate of 0.25 s/scan; and an electron multiplier (EM) voltage of 3000 V. Spectra of the volatile profile were compared to a mass spectral database from the NIST V.14 Llibrary values (Palisade Corp., Newfield, NY, USA). There were 3 replications for each analysis.

2.5. Calculation of Volatile Compounds. Each volatile compound of the clear peak from the GC-MS chromatogram was analyzed for the content compared to thiophene as the internal standard. Volatile content in ng thiophene per g fresh weight was estimated by the peak area of volatiles divided by the peak area of internal standard (thiophene) and 10 μL internal standard solution (0.5 g·L^{-1} thiophene) to 5 g durian homogenate prior to taking SPME [11].

$$\text{Volatile content}\left(\text{ng thiophene g}^{-1}\text{FW}\right) = \frac{\text{peak area of volatile/peak area of internal standard}}{\text{g durian aril homogenate}}. \tag{1}$$

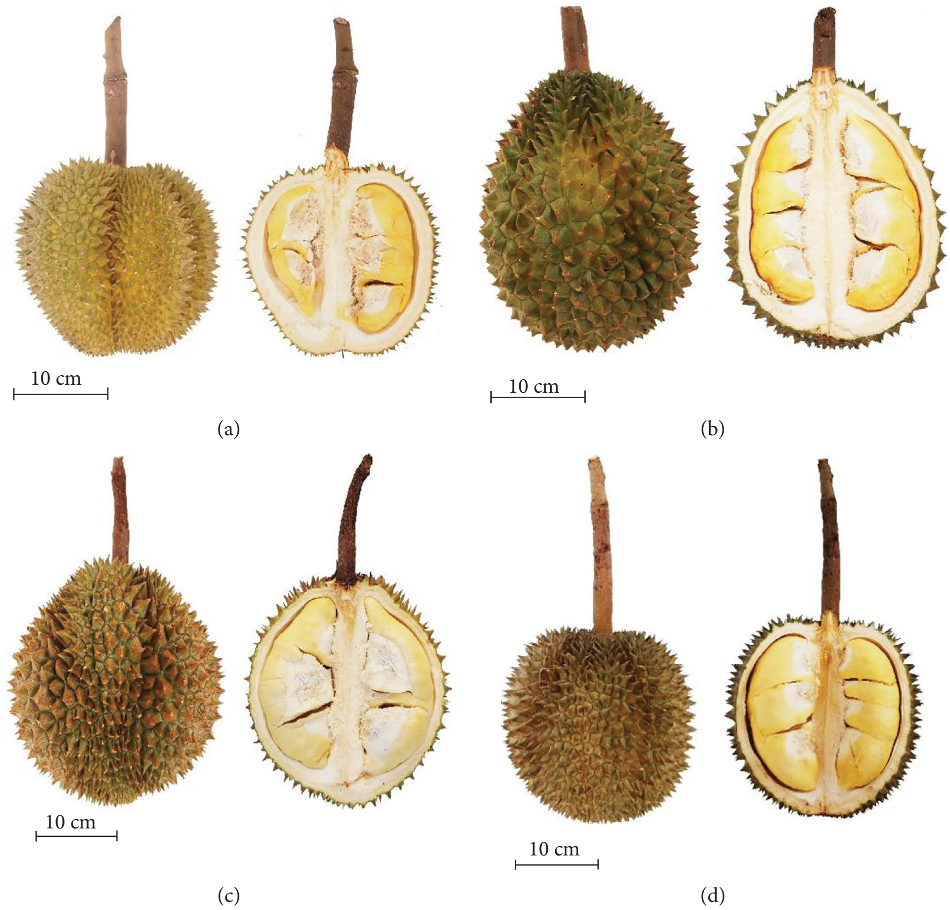


Figure 1: Appearances of the whole fruit (left) and flesh (right) of (a) "Chanthaburi 1," (b) "Chanee," (c) "Monthong," and (d) "Kanyao."

Odor activity value (OAV) was obtained by dividing the concentration of the compound in a matrix by its odor threshold in that matrix. Thus, it is generally assumed that the odorants with higher OAVs contribute more strongly to the overall aroma. OAV of each volatile compound was calculated using the following formula [12]:

$$\mathrm{OAV} = \frac{\text{concentration of the volatile content}}{\text{odor theshold value}}. \quad (2)$$

2.6. Statistical Analysis. The volatile relationship of durian cultivars was analyzed using principal component analysis (PCA) by Minitab® program ver.17 (Minitab Ltd., UK). The contents and types of ester volatiles between cultivars were analyzed using multivariations of principal components by Minitab®.

3. Results and Discussion

3.1. Volatile Profiles in Ripe Durians. From our experience, here was the first report of volatiles contributed in ripe flesh of "Kanyao," and a new hybrid, "Chanthaburi 1" bred from "Chanee" as the female gamete and "Monthong" as the male gamete. There were 41 major volatile compounds detected in 4 cultivars, comprising 33 esters, 2 sulfur-containing compounds, 3 organic acids, 2 phenolics, and 1 aldehyde (Table 1). "Chanthaburi 1" contained major 16 volatiles of 14 esters and 2 sulfur compounds. "Chanee" contained mainly 21 compounds of 17 esters, 3 organic acids, and 1 aldehyde. "Monthong" comprised 23 compounds of 19 esters and 2 sulfur compounds and 2 organic acids. "Kanyao" found 29 volatiles, including 23 esters, 1 sulfur compound, 1 phenolic acid, 3 organic acids, and 1 aldehyde.

Fruit odor is a mixture of many volatile substances, but the main volatile component is the criteria used to determine the odor matter. Nowadays, the odor threshold value of that substance is academically used and can be described, whereas OAV is calculated from the detected substance. The OAV value greater than 1 is the more important [13]. From OAV, ethyl-2-methylbutanoate (277.3), ethyl nonanoate (225.7), ethyl octanoate (204.9), and ethyl hexanoate (115.0) were the active volatiles of "Chanthaburi 1" ripe flesh, whereas diethyl disulfide was only 4.0 (Table 2). In "Chanee" flesh, 5 ethyl esters, ethyl octanoate (3613.6), ethyl dodecanoate (1126.2), ethyl-2-methylbutanoate (923.2), ethyl hexanoate (318.5), and ethyl propanoate (117.0), were among the major active volatiles (Table 2). In "Monthong" ripe flesh, ethyl octanoate (4173.7), ethyl hexanoate (1808.8), methyl octanoate (843.3), and ethyl-2-methylbutanoate (278.3) were high in the OAV (Table 2), while ethyl octanoate (4241.9), ethyl dodecanoate

Table 1: Volatile compounds released from ripe flesh of 4 Thai durian fruits corresponded to the GC-MS chromatogram profiles.

	Compound	RT	Relative content (ng thiophene/g FW)			
			"Chanthaburi 1"	"Chanee"	"Monthong"	"Kanyao"
			Ester			
1	Methyl-2-methylbutanoate	0.4766	nd	nd	0.71	nd
2	Ethyl acetate	2.1226	8.81	nd	nd	nd
3	Ethyl propanoate	2.9628	nd	3.39	nd	5.70
4	Ethyl-2-methylpropanoate	3.6143	1.85	5.32	2.85	9.71
5	Ethyl butanoate	4.3402	nd	1.08	2.07	2.69
6	Propyl propanoate	4.5230	nd	nd	nd	2.38
7	Ethyl-2-methylbutanoate	5.3346	83.20	276.97	83.49	198.86
8	Methyl-2-methyl-2-butenoate	5.7576	4.67	1.11	1.08	1.07
9	Methyl hexanoate	5.7747	nd	nd	nd	7.33
10	Ethyl-3-methyl-2-butenoate	6.5005	4.74	4.98	1.51	nd
11	Propyl-2-methylbutanoate	6.5348	nd	45.52	nd	nd
12	Ethyl-2-methyl-2-butenoate	7.5865	50.87	8.30	nd	6.61
13	Pentyl-2-methylbutanoate	7.7465	26.58	nd	nd	63.31
14	Methyl-2-hexenoate	8.3524	nd	nd	0.59	nd
15	Ethyl hexanoate	9.2496	10.35	28.67	162.79	65.76
16	Methyl heptanoate	9.9754	nd	1.93	nd	nd
17	Ethyl-2-methylpentanoate	10.227	nd	5.82	nd	nd
18	Propyl-2-methyl-(E)-2-butenoate	10.296	16.93	nd	nd	3.17
19	Ethyl-2-hexenoate	10.547	1.05	nd	7.62	1.32
20	Propyl hexanoate	11.999	nd	nd	18.92	10.29
21	Ethyl heptanoate	12.096	nd	15.50	8.20	8.93
22	Methyl octanoate	12.850	nd	nd	21.08	26.94
23	Ethyl-4-octenoate	14.548	nd	nd	3.23	nd
24	Ethyl octanoate	14.931	8.20	144.54	166.95	169.68
25	Ethyl-2-methyl octanoate	15.754	nd	3.16	nd	0.80
26	Ethyl-(E)-2-octenoate	16.302	0.85	nd	11.35	3.10
27	2-Methylbutyl hexanoate	16.463	nd	nd	1.16	nd
28	Propyl octanoate	17.543	nd	5.81	10.61	16.20
29	Methyl decanoate	18.400	nd	nd	3.08	5.99
30	Ethyl decanoate	20.252	2.93	4.37	24.15	27.25
31	Methyl dodecanoate	23.424	nd	nd	nd	1.78
32	Ethyl dodecanoate	25.064	nd	2.25	nd	8.28
33	Ethyl nonanoate	25.076	2.26	nd	nd	nd
	Total		223.29	558.74	531.44	647.13
			Sulfur compound			
1	Diethyl disulfide	7.0606	4.69	nd	2.48	nd
2	3,5-Dimethyl-1,2,4-trithiolane	13.074	5.10	nd	1.14	1.66
	Total		9.79	0	3.61	1.66
			Acid			
1	Propanoic acid	2.7227	nd	1.02	nd	2.91
2	Hexanoic acid	8.8038	nd	0.72	4.45	9.92
3	Octanoic acid	14.302	nd	3.47	2.86	12.57
	Total		0	5.21	7.31	25.40
			Phenolic			
1	2,4-Di-tert-butylphenol	23.138	nd	nd	1.72	nd
	2,5-bis (1,1-Dimethylethyl phenol)	23.144	nd	nd	nd	1.80
	Total		0	0	1.72	1.80
			Aldehyde			
1	trans-2-Methyl-2-butenal	3.4086	nd	4.36	nd	9.61
	Total	3.4086	0	4.36	0	9.61

(4138.9), methyl octanoate (1077.4), ethyl hexanoate (730.6), ethyl-2-methylbutanoate (662.9), and ethyl propanoate (196.4) were the active volatiles in "Kanyao" (Table 2). There were some volatile compounds detected only in each cultivar. Ethyl acetate (10.0) and ethyl nonanoate (225.7) were only in "Chanthaburi 1," propyl-2-methylbutanoate (n/a), methyl heptanoate (6.7), and ethyl-2-methyl pentanoate (n/a) were only in "Chanee," methyl-2-methylbutanoate (n/a), methyl-2-hexenoate (n/a), ethyl-4-octenoate (n/a), and 2-methylbutyl hexanoate (n/a) were only in "Monthong," and propyl propanoate (8.5), methyl hexanoate (<1), and methyl dodecanoate (683.3) were only in "Kanyao."

Table 2: Odor characteristics of ester, sulfur, acid, phenolic, and aldehyde containing compounds from ripe flesh of 4 Thai durian fruits.

	Compound	Odor description	Aroma threshold values (ppb)	Odor activity values (OAV)				References*
				"Chanthaburi 1"	"Chanee"	"Monthong"	"Kanyao"	
			Ester					
1	Methyl-2-methylbutanoate	Sweet, fruity, apple-like odor	n/a	—	—	n/a	—	—
2	Ethyl acetate	Fruity, sweet, grape- and rum-like odor	0.88	10.014	—	—	—	D
3	Ethyl propanoate	Green, fruity apple-like odor	0.029	—	117.048	—	196.40	M
4	Ethyl-2-methylpropanoate	Fruity	0.1	18.50	53.163	28.47	97.05	O
5	Ethyl butanoate	Fruity, pineapple	0.2	—	5.38	10.35	13.44	H
6	Propyl propanoate	Sharp, chemical, pungent, sweet, fruity	0.28	—	—	—	8.48	M
7	Ethyl-2-methylbutanoate	Fruity	0.3	277.329	276.97	278.31	662.88	N
8	Methyl-2-methyl-2-butenoate	Caramel note, ethereal rum	35 (in water)	<1	<1	<1	<1	R
9	Methyl hexanoate	Fruity, pineapple, ethereal	70	—	—	—	<1	O
10	Ethyl-3-methyl-2-butenoate	n/a	n/a	n/a	n/a	n/a	—	—
11	Propyl-2-methylbutanoate	Winey	n/a	—	n/a	—	—	—
12	Ethyl-2-methyl-2-butenoate	Sweet fruity, green notes	n/a	n/a	n/a	—	n/a	—
13	Pentyl-2-methylbutanoate	n/a	12	2.22	—	—	5.28	A
14	Methyl-2-hexenoate	Fruity green banana honey	n/a	—	—	n/a	—	—
15	Ethyl hexanoate	Apple-like, fruity, aniseed-like, sweet	0.09	115.032	318.54	1,808.81	730.63	H
16	Methyl heptanoate	Sweet, fruity and green, with a waxy apple-like note	0.29	—	6.67	—	—	B
17	Ethyl-2-methyl pentanoate	Fruity, green, melon and waxy with a fatty nuance	n/a	—	n/a	—	—	J
18	Propyl-2-methyl-(E)-2-butenoate	n/a	n/a	n/a	—	—	n/a	—
19	Ethyl-2-hexenoate	Fruity, green, pulpy pineapple and apple	0.14	7.462	—	54.41	9.46	C
20	Propyl hexanoate	Sweet, fruity, juicy, pineapple, green and tropical	70	—	—	<1	<1	E
21	Ethyl heptanoate	Fruity pineapple cognac rum wine	0.24	—	64.60	34.16	37.22	D
22	Methyl octanoate	Waxy, green, sweet, orange, aldehydic, vegetable, herbal	0.025	—	—	843.29	26.94	I
23	Ethyl-4-octenoate	n/a	n/a	—	—	n/a	—	—
24	Ethyl octanoate	Pleasant, fruity, floral odor, wine apricot note	0.04	204.91	3,613.61	4,173.69	1,077.42	K
25	Ethyl-2-methyl octanoate	n/a	n/a	—	n/a	—	n/a	—
26	Ethyl-(E)-2-octenoate	Fruity, green with a fatty waxy note	n/a	n/a	—	n/a	n/a	—
27	2-Methylbutyl hexanoate	Ethereal	n/a	—	—	n/a	—	—
28	Propyl octanoate	n/a	n/a	—	n/a	n/a	n/a	—
29	Methyl decanoate	Oily, winey, fruity, floral	n/a	—	—	n/a	n/a	—
30	Ethyl decanoate	Fruity, grape-, cognac-, and brandy-like odor	0.53	5.53	8.25	24.15	51.42	F

Table 2: Continued.

	Compound	Odor description	Aroma threshold values (ppb)	Odor activity values (OAV)				References*
				"Chanthaburi 1"	"Chanee"	"Monthong"	"Kanyao"	
31	Methyl dodecanoate	Waxy, soapy nutty, coconut, mushroom	0.0026	—	—	—	683.31	B
32	Ethyl dodecanoate	Waxy, soapy, rummy, nutty, floral	0.002	—	1,126.15	—	4,138.90	B
33	Ethyl nonanoate	Slightly fatty, oily, fruity, nutty, reminiscent of cognac with a rosy fruity note	0.01	225.68	—	—	—	L
			Sulphur compound					
1	Diethyl disulfide	Onion, garlic	2	3.97	—	1.25	—	M
2	3,5-Dimethyl-1,2,4-trithiolane	Sulphury, onion, meaty	n/a	n/a	—	n/a	n/a	G
			Acid					
1	Propanoic acid	Pungent, acidic, dairy	1	—	1.02	—	2.94	P
2	Hexanoic acid	Sour, fatty, sweaty, cheesy	0.0047	—	154.23	956.57	2,132.40	Q
3	Octanoic acid	Fatty, waxy, rancid oily, vegetable cheesy	0.011	—	318.60	262.70	1,154.29	Q
			Phenolic					
1	2,4-Di-tert-butylphenol	n/a	n/a	—	—	n/a	—	—
2	2,5-bis (1,1-Dimethylethyl phenol)			—	—	—	n/a	—
			Aldehyde					
1	trans-2-Methyl-2-butenal	Strong green fruit	n/a	—	n/a	—	n/a	G

*The capital letters represented the references of odor threshold value as follows: [A][14] Allison and Katz (1919), [B][15] Backman (1917), [C][16] Berger (1985), [D][17] Cometto-Muñiz, et. al. (2005), [E][18] Fan and Xu (2011), [F][19] Ferreira et. al. (1998), [G][20] Gemert (2011), [H][21] Guth (1997), [I][22] Karl et. al. (1994), [J][23] Komthong (2006), [K][24] Rychlik (1998), [L][25] Schwarz (1995), [M][26] Nagata (2003), [N][27] Takeoka et al. (1989), [O][28] Takeoka et al. (1990), [P][29] van Thriel et al. (2006), [Q][30] Wise et al. (2007), and [R][31] Yair (2012).

Ripe flesh of most durian cultivars contains ethyl-2-methylbutanoate (fruity note) and ethyl hexanoate (fruity, apple, green, and tropical fruit odor) as the active volatiles showing high OAV. Both found in all four cultivars and most commercial durians were blended with some high-OAV compounds to characterize the flavor of each durian variety. In general, ripe durian flesh exhibits the fruity sweet fragrance of both compounds. "Chanthaburi 1" contained fewer components of volatiles as well as low OAV of the volatiles. This indicates that the flesh of "Chanthaburi 1" conducted very low intensity of odors during ripening. Ethyl heptanoate (fruity, pineapple, banana-like note) was found in every cultivar except "Chanthaburi 1." Ripe flesh of "Chanee" exhibited the strongest durian aroma among 4 varieties: "Chanee" exhibited aroma of ethyl octanoate (fruity, floral odor, wine apricot note), ethyl dodecanoate (waxy, soapy, nutty, rummy), and ethyl propanoate (green fruity, apple-like) characterized as nutty, rummy, and green apple-like, "Monthong" exhibited strong apple-like fruity, aldehydic, waxy fragrance of ethyl octanoate (fruity, floral odor, wine apricot note), ethyl hexanoate (apple-like, fruity), and methyl octanoate (waxy, green, sweet, orange, aldehydic vegetable), and "Kanyao" exhibited more complex waxy, nutty, green apple-like fruity aroma of ethyl octanoate, ethyl dodecanoate (waxy, soapy, nutty, rummy note), methyl octanoate (waxy, green, sweet orange), and ethyl propanoate (green fruity, apple-like).

Diethyl disulfide and 3,5-dimethyl-1,2,4-trithiolane found in low levels in ripe durian pulp are the key compounds in durians. Although sulfur-containing compounds exhibited low OAV, compared to the esters, they exhibit an annoying pungent smell. "Chanthaburi 1" as well as "Monthong" contained sulfur-containing compounds of diethyl disulfide and 3,5-dimethyl-1,2,4-trithiolane, which exhibit a garlic-like, onion-like, pungent smell [32]. In particular, diethyl disulfide in ripe "Monthong" showing an OAV of 1.25 would release the pungent smell of "Monthong" durian as reported by Laohakunjit et al. [8] and Niponsak et al. [9]. Previous studies in Malaysia and Indonesia found that the indigenous varieties exhibited a prominent smell of sulfur-containing compounds when fully ripe showing an unpleasant odor overall [32, 33].

In 4 cultivars of Thai durian fruit, ripe aril sharply produced a series of ethyl esters derived from ethyl alcohol and acyls CoA of straight carbons ranging from C_4–C_{10} (Table 1). Ethanol in the aril could be generated from anaerobic respiration under a partial hypoxic condition in aril tissue. Due to very high respiration of durian fruit during ripening, fruit husk behaving like a gas barrier makes low gas permeability to the aril. Under partial hypoxia, anaerobic respiration was induced in the aril, resulting in increased ethanol [34–37]. Aliphatic and aromatic alcohols are typically found in Malaysian durians, whereas thiols are produced in Thai durians and alcohols are not typically produced in Indonesian and Filipino durians [37]. On the other hand, with a series of straight acyl CoA reacted with the ethanol, it is supposed that β-oxidation of fatty acids would be involved in the process of ripe fruits [38] as durian pulps have high contents of fatty acids such as methyl stearate (35.93%), methyl palmitate (32.91%), methyl palmitoleate (9.50%), methyl octadecenoate (4.86%), methyl oleate (4.68%), methyl myristate (2.52%), and methyl linoleate (2.20%) [39]. Furthermore, amino acid metabolism plays a crucial role in ester production in durians. For instance, ethyl-2-methylbutanoate, a primary volatile compound, is derived from 2-methylbutanoyl-CoA through isoleucine metabolism [40]. The origination of acyls CoA in the ester production could be separated into two sources from the results. When the acyl CoA of C_4 could be derived from amino acids, acyl CoA above C_6 could be from lipid oxidations. Furthermore, alcohol acyltransferase (AAT), which modifies alcohols and acyl CoA to esters, could be essentially involved in the production of esters in most durians. Although ATT has not yet been reported in durian, it was reported to be essential for ester production during ripening in many fruits [41–43]. However, as a result of fewer esters in “Chanthaburi 1,” the production of esters is apparently disturbed in the fruit probably by mutant functioning of the AAT or the substrate-enzyme incompatibility.

3.2. The Relationship of Durian Cultivar Relied on Aroma Volatiles. All 4 varieties showed that ethyl esters were the major components in the ripe flesh. Ethyl acetate and ethyl nonanoate were found in “Chanthaburi 1” but not in the parent, “Chanee” and “Monthong,” whereas, on the other hand, ethyl butanoate and ethyl heptanoate found in the parent were not found in “Chanthaburi 1”. Methyl-2-methylbutanoate was detected only in ripe “Monthong” flesh.

Ester compounds as the major volatiles were taken to calculate the relationship between cultivars. The differences in essential substances between durian species may be due to genetics and the environment. Genetic factors influence the formation of precursors, enzymes, and odor generation [44]. The durian of “Chanthaburi 1,” a hybrid variety, has overall odor characteristics related to the parent variety, “Chanee,” and the father species is “Monthong.” Nevertheless, by considering the odor, “Chanthaburi 1” has a mild odor while still unripe, similar to the odor of “Kanyao.” Although identifying the essential substances in “Chanthaburi 1” durian exhibited a more minor odor type than the strong aroma varieties, the essential substances (OAV) in the “Chanthaburi 1” exhibited characteristics related to both “Chanee” and “Kanyao.” The relative content of the ester was obtained according to the dendrogram (Figure 2) of each essential substance. The volatile contents in “Chanthaburi 1” were related to “Monthong” when considering the ester composition. The ester compounds in “Chanthaburi 1” were correlated well with the “Monthong” variety, consistent with the species characteristics that ‘Monthong’ was the father. However, the relationship of ester compounds in “Chanee” was close to that in “Kanyao.”

Principal component analysis (PCA) using the ester compounds from Table 1 was operated to correlate and classify the essential components of the four durian varieties. Ester compounds were classified in the same component, with an eigenvalue greater than 1, and the component was equal to 2 (data not shown) with Minitab© 17 displayed in the score plot and biplot (Figure 3). The main component and the secondary components were associated with the ester compounds of the four durian varieties. When looking at the main components, “Chanthaburi 1” durian was related to “Chanee,” and from the secondary, “Chanthaburi 1” was, on the other hand, related to the “Monthong” variety which corresponds to the ester characteristics of the parents. But, “Kanyao” has characteristics that are clearly different from those of “Chanthaburi 1” by both components. In addition, the ester characteristics of “Chanthaburi 1” as shown in Figure 3(c) were ethyl acetate, ethyl nonanoate, and methyl-2-methyl-2-butenoate, which exhibit a rum-like, grape, and cognac, as well as caramel note. For “Chanee,” it can be seen from Figure 3(c) that the distinctive esters were propyl-2-methylbutanoate, ethyl-2-methyl pentanoate, and methyl heptanoate showing winey, apple, pineapple, green, melon and waxy flavors, cognac rum wine, intensely fruity, and orris-like. In “Monthong,” the ester characteristics were methyl-2-methylbutanoate, ethyl-2-hexenoate, and methyl-2-hexenoate. The scent characteristics are sweet fruity, apple-like odor, green, pineapple, apple, green, banana, honey. On the other side, “Kanyao” exhibited a distinctive scent of methyl hexanoate, propyl propanoate, and methyl dodecanoate, showing fruity, pineapple, complex fruity odor, apple and banana, waxy soapy, nutty, and coconut mushroom. When considering the OAV value of each durian species, if the OAV is greater than 1, it can be expected to exhibit a unique aroma. The OAV value of “Chanthaburi 1” was clearly similar to that of “Chanee,” the mother variety, and close to that of “Kanyao” (Table 2 and Figure 4). The OAV values showed that “Chanthaburi 1” had the dominant esters, ethyl acetate (10.0) and ethyl nonanoate (225.7), which exhibited fruity, sweet, grape and rum-like, slightly fatty, oily, fruity, scent characteristics of nutty, reminiscent of cognac with a rosy fruity note. Nevertheless, “Kanyao” has outstanding OAV values of ethyl octanoate (4,241.9) and ethyl dodecanoate (4,138.9) at high, which is likely to be another distinctive scent, characterized by long stems showing fruity, fatty, floral odor (wine apricot note), waxy, sweet, musty, pineapple, dairy, sweet, waxy soapy rummy, and nutty floral. The distinctive OAV value is of methyl heptanoate (6.7) because it is found only in “Chanee,” showing sweet, fruity, and green, with a waxy apple-like note. The higher levels of OAV were found in “Monthong” and “Kanyao” durians, but less common in “Chanthaburi 1” was ethyl octanoate (204.9), which showed a pleasantly fruity, floral odor (wine apricot note). The OAV values were different from the ester relative content, which was the relative content of the volatile compounds present in each durian species, indicating that “Chanthaburi 1” was

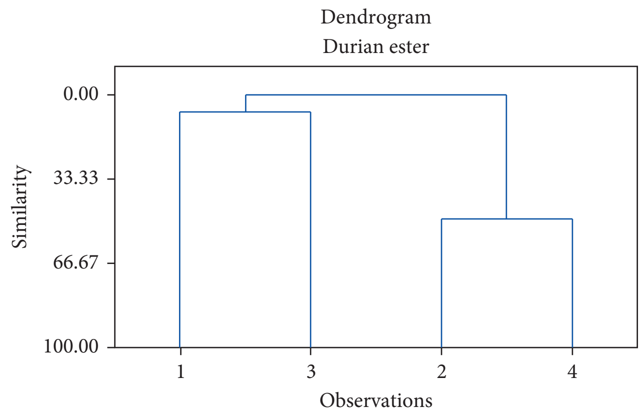
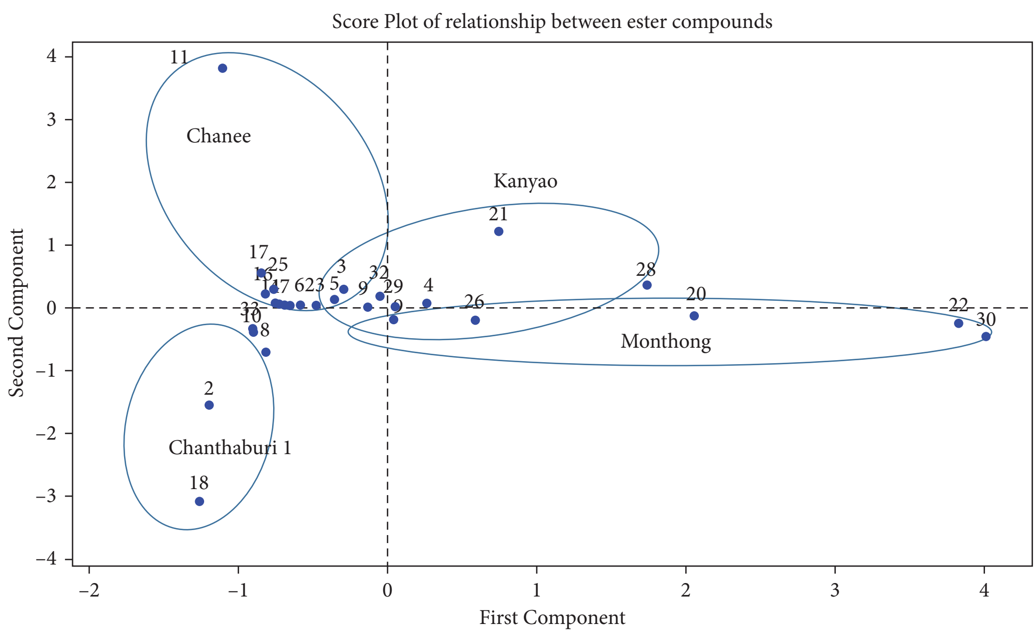
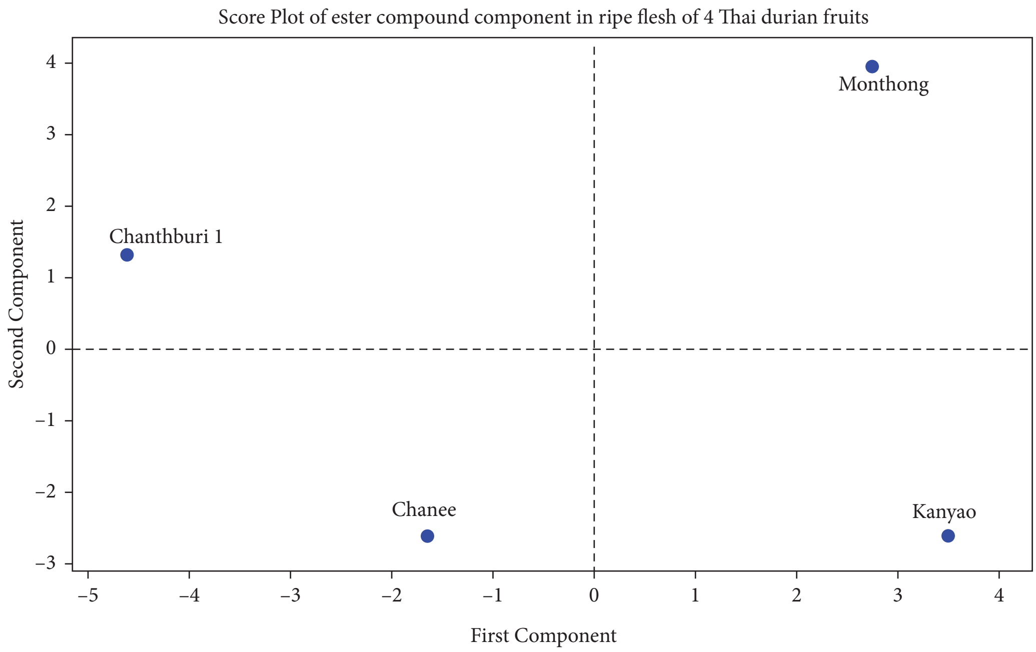


Figure 2: Dendrogram of the relationship in the ester compound produced in 4 Thai durian cultivars (1 = "Chanthaburi 1," 2 = "Chanee," 3 = "Monthong," and 4 = "Kanyao").

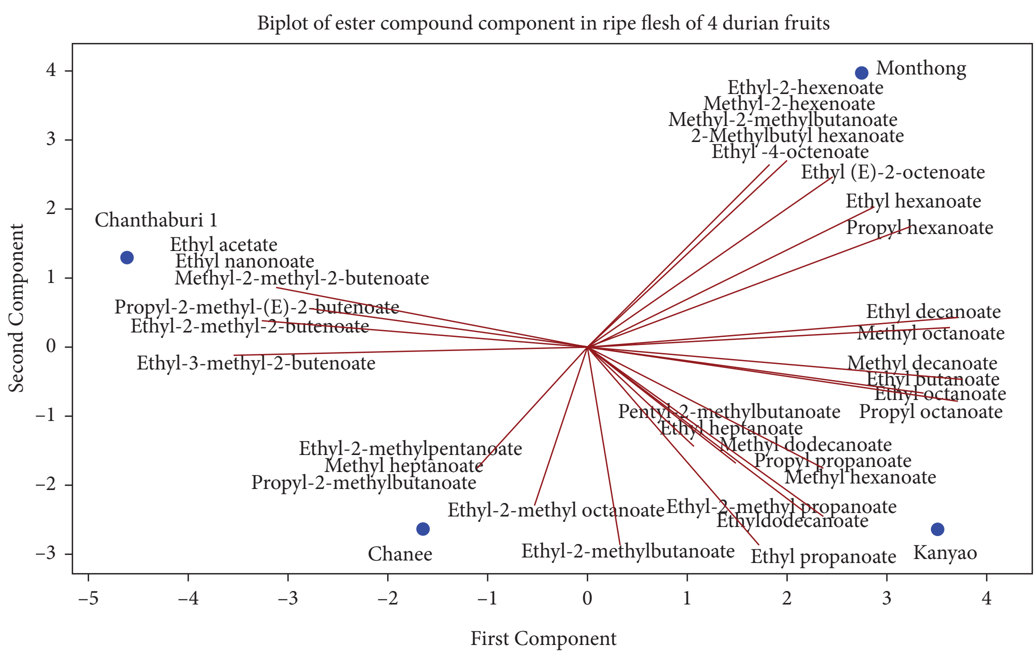


(a)

Figure 3: Continued.



(b)



(c)

Figure 3: Principal component analysis (PCA) relationship between 4 Thai durian cultivars. (a) Score plot of the relationship between 4 Thai durian cultivars using the ester compounds. (b) Score plot of the ester compound component in ripe flesh of 4 Thai durian cultivars. (c) Biplot of the ester compound component relationship with 4 Thai durian cultivars.

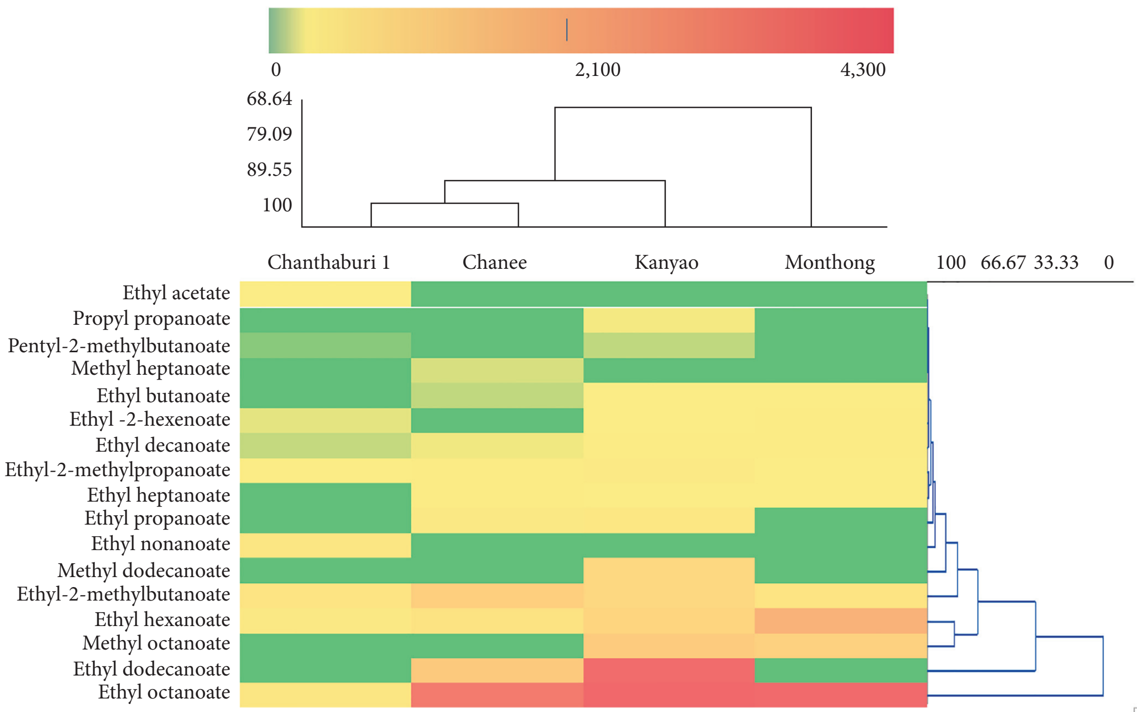


Figure 4: Heat map of odor activity value (OAV), which is greater than 1 of each durian species.

consistent with "Monthong" and "Chanee," the father and mother, respectively. Nevertheless, if the OAV value was considered, "Chanthaburi 1" was close to "Kanyao" more than "Monthong" (Figure 4). According to the observation from the odor characteristics, the odor of "Chanthaburi 1" is mild, similar to that of "Kanyao," which the OAV value can explain to some extent. Based on information on the composition of these essential substances, it could greatly benefit the status of Thai durians in terms of the choice of eating fresh fruit and the choices to use ripe durian pulp as an ingredient of food or dessert which requires the durian odor. The study could increase the opportunities of Thai durian transport channels to the world.

4. Conclusions

Thirty-three esters and three sulfur-containing compounds were the main volatiles found and affected the flavor character of the ripe pulp of four varieties of Thai durians, "Chanee," "Monthong," "Kanyao," and "Chanthaburi 1." Ethyl esters were the major esters as ethyl-2-methylbutanoate and ethyl hexanoate were the crucial essential substances found in all four varieties. The overall aroma character of the durian was a mixture combined of fruity-like apple/pineapple with rum, butter, oily, and waxy odors. Although ripe durians produced few sulfur-containing volatiles, the compounds exhibit a sulfurous pungent smell. Using the volatile ester profiles, "Chanthaburi 1" correlated with "Chanee," the mother breed, and "Monthong," the father breed. "Kanyao" was different from "Chanthaburi 1." However, with high OAV values concerned, "Chanthaburi 1" was obviously associated with "Chanee," but the odor character was more similar to "Kanyao" than "Monthong."

Data Availability

The data used to support the findings of this study are included within the supplementary information file.

Conflicts of Interest

There are no conflicts of interest in this study.

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Supplementary Materials

Supplementary Figure 1: naturally ripe fruit at the initial dehiscence (red circle) at the blossom end. (*Supplementary Materials*)

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