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Influence of maturity and postharvest treatment on the volatile profile and physiological properties of the durian (*Durio zibethinus* Murray) fruit

[1*]Maninang, J. S., [2]Wongs-Aree, C., [1]Kanlayanarat, S., [1]Sugaya, S. and [1]Gemma, H.

[1]*Pomology Laboratory, Graduate School of Life and Environmental Sciences, University of Tsukuba, Tennodai, Tsukuba, 305-8577 Ibaraki, Japan*
[2]*Division of Postharvest Technology, School of Bioresources and Technology, King Mongkut's University of Technology Thonburi, Bangkok 10140 Thailand*

Abstract: Variation in the volatile profile and physiological properties of durian (*Durio zibethinus* Murray cvs. Monthong and Chanee) were examined in fruits harvested at 100% (abscised) or 75-85% maturity, with the latter further subjected to various postharvest practices (i.e. Ethephon or 1-methylcyclopropene treatment followed by low temperature storage at 15°C, 75% RH). Consistent with literature, abscised and untreated 75-85% fruits kept in ambient condition (28°C, 75% RH) were the earliest to reach full maturity (dehiscent stage), with dehiscence observed a day earlier in Chanee for both maturities. Fruits kept in low temperature storage have delayed dehiscence, but exhibited the typical climacteric and normal ripening when transferred to ambient condition. Pulp texture of the fruits in all treatment groups reached the same degree of firmness upon dehiscence. Volatile profile analysis of dehiscent fruits by headspace solid phase microextraction coupled with gas chromatography-mass spectrometry revealed cultivar-specific variations. In Monthong, abscised and untreated 75-85% mature fruits ripened in ambient condition produced comparable levels of the major volatiles, while in Chanee, the levels of sulfur-containing compounds were decreased in 75-85% mature fruits. Ethephon-treated Chanee fruits kept in low temperature storage and transferred to ambient condition produced all the sulfur-containing volatiles upon dehiscence, while the 1-MCP-treated fruits were only detected of diethyl disulfide. Interestingly in Monthong, sulfur-containing volatiles production appears to be abolished in all fruits kept in low temperature storage. But, keeping these fruits for three more days in ambient condition recovered their capacity to produce the sulfur-containing compounds. On the other hand, all the major ester compounds were detected in all treatment groups, with the concentration of ethyl 2-methyl butanoate apparently enhanced in ethephon-treated fruits of both cultivars. The production of sulfur-containing volatiles exhibits a cultivar-specific sensitivity to low temperature storage and 1-MCP application. With further investigation, studies along this line may provide basis for the control of sulfur-containing volatiles in durian by the use of postharvest interventions.

Keywords: Durian, diethyl disulfide, volatiles, sulfur compounds, esters, 1-Methylcyclopropene, ethephon

Introduction

Durian (*Durio zibethinus* Murray) is the most famous and economically important tropical fruit in South East Asia. Production and export of the fruit remains predominated by Thailand which mainly produces the cultivars Chanee and Monthong (Subhadrabandhu and Ketsa, 2001; Somsri and Vichitrananda, 2007). Harvest and postharvest practices for durian vary among durian producing countries, and depend on the target market for the produce. In Thailand, durian is usually harvested from the tree at 75-85% maturity. Practically all export-bound fruits are treated with Ethephon (2-Chloroethylphosphonic acid), an exogenous ethylene source, to promote even ripening, and are transported in low temperature storage (15ºC, 95% RH) for seven to ten days (personal communication with Chantaburi Horticultural Research Center, Thailand). While, fruits for the local market are not treated with Ethephon, usually more mature (90% to 100% maturity), and are transported and allowed to ripen at ambient conditions (28-30°C, 75% RH). Low temperature storage alone is not a common postharvest practice by the industry for durian.

Statistics reflect a short-distance movement in trade of the fresh fruit mainly to neighboring Asian markets limited by its high perishability (Somsri and Vichitrananda, 2007). More distant markets like the US, Australia and Canada which continue to strengthen, are mainly supplied with frozen durian. Among the postharvest interventions being explored to prolong the storage life of climacteric fruits, the use of the ethylene antagonist 1-methylcyclopropene

*Corresponding author.
Email: *john.maninang@up.edu.ph*
Tel: +81 29 8534819; Fax: +81 29 8537225

(1-MCP) has been most promising. It has been proven to be effective in prolonging the shelf life of Packham's Triumph pears in cold storage (up to six months), also a climacteric fruit, while maintaining the desired characteristics and the capacity for volatile production when transferred to ambient conditions (Moya-León *et al*., 2006). Similar results have also been reported in apples (Bai *et al*., 2005; Defilippi *et al*., 2005) and conference pears (Rizzolo *et al*., 2005). In durian, the use of 1-MCP as a postharvest intervention has not been approved. Moreover, the optimum conditions for its successful use still need to be established.

Durian has gained popularity not only for its delicious taste, but for its strong odor (Nanthachai, 1994). It is believed that harvesting practices and postharvest handling affect the aroma and flavor of durian upon ripening. Nanthachai *et al*. (1994) indicated that durian fruits that naturally abscised from the tree (100% mature) and allowed to ripen develop a fuller aroma and taste, which is preferred by the markets in Malaysia, Indonesia and the Philippines compared to those that are plucked from the tree and ripened. However, no study has yet linked existing industry practices to variations in concentration of the volatile constituents in the fruit. Moreover, the effect of emerging postharvest technologies on the flavor and aroma compounds like the application of 1-MCP has been menially explored in durian. Using headspace solid phase microextraction (HS-SPME) method coupled with gas chromatography-mass spectrometry (GC-MS), the present study describes the influence of existing harvest and postharvest practices on the profile and concentration of the volatile constituents of durian in association with the physiological changes of the fruit upon ripening.

Materials and Methods

Durian fruit

A total of 48 durian fruits of cultivars Chanee (N = 24) and Monthong (N = 24) used were obtained from the orchard of Chantaburi Horticultural Research Center, Thailand. As such, these fruits were subjected to uniform cultural practices and environmental conditions during production. Fruit maturity was determined by experts by tapping, and visual inspection. The fruits were all collected in May 2010 and transported within 12 h to King Mongkut's University of Technology Thonburi, Bangkok, Thailand where treatments and experimental procedures were conducted.

Treatments

All fruits were dipped in fungicide solution [Imazalil, Latda Co. Ltd., Bangkok, Thailand; active ingredient – allyl-1-(2,4-dichlorophenyl)-2-imidazole-1-ylethyl ether; 40 ml/20 l water, 5 min]. For each cultivar, naturally abscised fruits (n = 6), and mature fruits (75-85% mature, N = 18) were selected for uniformity of size and freedom from visual defects. Two of the abscised fruits and three of the 75-85% mature fruits were analyzed of initial pulp texture. The mature fruits were further assigned to three subgroups: untreated (n = 5); treated with Ethephon (n = 5); and treated with 1-MCP (n = 5). Both abscised and untreated mature fruits were allowed to ripen in ambient conditions (28ºC, 75% RH) based on the practice of local traders.

Ethephon (Tapesiam Ltd. Co., Samat Prakran, Thailand; active ingredient – chloroethyl phosphoric acid, 48% w/v) diluted to 1:1 (v/v water) was applied on the freshly cut peduncle of mature fruits which were transferred and kept in cold storage (15ºC, 95% RH) for 9 days consistent with the common practice of durian exporters. The Ethephon-treated fruits were then transferred to ambient conditions until dehiscence.

Fruits were exposed to 1-MCP (Ethy Bloc, Floralite Inc., SC 29488, USA) at 50 ppm for 6 h, 20ºC, kept in cold storage (15ºC, 95% RH) for 16 d, and transferred to ambient conditions until dehiscence. The 1-MCP treatment conditions were based on the recommendations in preliminary studies of the Chantaburi Horticultural Research Center, Thailand.

To assure full ripeness of the fruits and allow for comparison across treatment groups, we used dehiscence as an indicator of the full table-ripeness and determinant of the end of storage life of durian in accordance with the report of Sriyook (1990) and Khurnpoon *et al.* (2008). Two fruits for each treatment group were segregated for monitoring daily ethylene and carbon dioxide production. These fruits were also analyzed of texture and volatile profile upon dehiscence in addition to the remaining fruits (two of abscised fruits; three for each treatment group of 75-85% mature fruits).

Respiration and ethylene production

All fruits were daily monitored of weight, respiration and ethylene production from the first day of postharvest storage through to dehiscence. Three representative fruits per group were individually placed in 4 L airtight containers fitted with gas sampling ports. After 1 h, 1 mL of gas samples were withdrawn from the headspace and quantified for carbon dioxide

and ethylene in a gas chromatograph equipped with TCD (model 4890 Agilent Technologies, Sta. Clara, California) and FID (model GC-18A, Shimadzu Co., Kyoto, Japan), respectively.

Pulp Firmness

Pulp obtained from fruits upon dehiscence was determined of firmness in a TA TX Plus Texture Analyzer (Stable Microsystems, Surrey, UK). A force of 5 kg was applied at a cross-head speed of 15 mm/min. The pre-test speed was set at 15 mm/min, while the test and post-test speed were set at 10 and 20 mm/min respectively. The force (N) required to insert the 6 mm diameter probe tip 0.5 cm deep into the pulp at 10 mm/min was recorded. Pulp firmness was also determined in non-dehiscent and post-dehiscent (3d after dehiscence) fruits in some treatment groups as indicated in the results and discussion section.

Isolation of volatile compounds using headspace-solid-phase microextraction (HS-SPME)

A 65 µm polydimethylsiloxane-divinylbenzene (PDMS/DVB) (Supelco Co., Bellefonte, PA, USA) was used in this study, as it was found most suitable according to Zhang and Li (2007). The fiber was conditioned prior to use according to suppliers instructions, 30 min at 250ºC. Fifty grams of durian pulp obtained from fruits upon dehiscence were homogenized with 100 ml distilled cooled water in an Ika T25 digital Ultra Turrax homogenizer (Ika, Germany) for 1 min at 7,000 rpm. Blended pulp (15 ml) was quickly transferred into a 30 ml vial. After equilibration for 40 min at 30ºC in a water bath, headspace sampling was performed at the same temperature for 30 min with stirring. Each sample was measured in triplicate at uniform conditions to minimize variation. Thiophene (15 µg) (Sigma, UK) was spiked into a separate sample as external standard for computation of concentration. All parameters in the procedure (i.e. weight of pulp, time of exposure of fiber to the headspace of the vial during microextraction and temperature) were kept constant to minimize variations among replicates.

Gas chromatography-Mass Spectrometry conditions

Desorption of the analytes from the fiber coating was done at the injection port of the GC at 250ºC for 5 min at a splitless mode. Volatile compounds were separated using HP-5MS capillary column (30 m × 0.25 mm id × 0.25 µm film thickness) (J&W Scientific Inc., Folsom, CA, USA). The oven temperature was initially set at 40ºC for 10 min, ramped to 250ºC at 5 ºC/min and held for 5 min. Purified helium (purity 99.999%) was used as the carrier gas at 1 ml/min. The MS was operated in SIM mode from m/z 30 to 550 at 2.1 spectra with 70 eV electron ionization at 230ºC, quadrupole at 150ºC. Data were analyzed using the RTE integration software (Agilent Technologies, Inc., Sta. Clara, CA, USA).

Identification of volatile compounds was initially accomplished by matching the mass spectra with the NIST v98 library values (Palisade Corp., Newfield, NY, USA). Only compounds with a similarity factor of more than 90% were chosen. Quantification of volatile compounds was carried out by comparing the peak areas of the analytes with that of thiophene.

Results and Discussion

Physiological changes, ripening and dehiscence of durian

Durian harvested in different maturities and subjected to different postharvest treatments showed markedly different patterns of respiration (Figure 1B and E) and ethylene evolution (Figure 1C and F) during storage. Between the abscised and untreated fruits, this difference appears to be partly attributable to the physiological status of the fruits. The initially soft texture of the pulp (Figure 2), and the high rates of ethylene and carbon dioxide production of abscised fruits that indistinguishably rose during storage reflect that these fruits were already in the late or post-climacteric stage. While in the untreated fruits (75-85% mature), climacteric ethylene evolution coincident with carbon dioxide production typical of durian (Siriphanich *et al*., 1994) was only observed during storage, confirming that these fruits were harvested at a pre-climacteric stage. Consistently, abscised fruits were the earliest to ripen and dehisce, a day earlier than the respective untreated fruits (Table 1). Chanee dehisced earlier than Monthong, except in the 1-MCP treatment group where both cultivars ripened simultaneously. Previous studies likewise noted earlier ripening of Chanee fruits than Monthong (Nanthachai, 1994; Subhadrabandhu and Ketsa, 2001). Chanee has been shown to ripen abnormally, if at all, when harvested at 75% maturity or less (Siriphanich *et al*., 1994). The successful ripening of the Chanee fruits in this study indicates that they were harvested at the appropriate maturity stage.

Fruits pretreated with either Ethephon or 1-MCP and stored in low temperature (15ºC, 95% RH) exhibited delayed climacteric, ripening and dehiscence. The physiological changes observed in these fruits during and after low temperature storage appear to be mainly influenced by the low temperature exposure itself, rather than Ethephon or 1-MCP

Table 1. Number of days to dehiscence of durian fruits in different treatment groups. Results are means ± SE of three replicate fruits.

Treatment	Fruit Maturity (%)	Storage Condition	No. of Days to dehiscence upon transfer to ambient condition		Total No. of Postharvest Days to Dehiscence	
			Monthong	Chanee	Monthong	Chanee
Abscised	100	28 ºC, 75 % RH			3	2
Untreated	75-85	28 ºC, 75 % RH			4	3
Ethephon	75-85	15 ºC, 96 % RH then 28 ºC, 75 % RH	5	3	14	12
1-MCP	75-85	15 ºC, 96 % RH then 28 ºC, 75 % RH	3	3	19	19

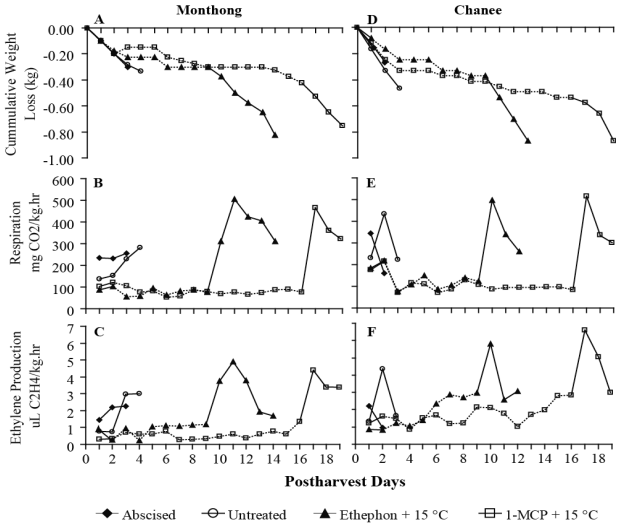

Figure 1. Changes in weight (A,D), respiration (B,E) and ethylene production (C,F) of whole durian fruits (Monthong and Chanee cultivars) in different treatments. Fruits were either kept in ambient conditions (__) or in cold storage (....) as described in the methodology. Results are means ± SE of duplicate fruits.

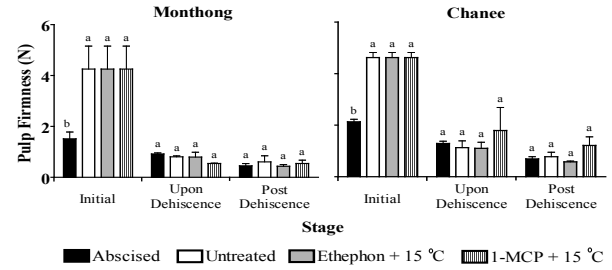

Figure 2. Pulp softening of durian fruits subjected to different treatments with reference to dehiscence. Results are means ± SE of duplicate fruits.

treatment. Although this observation needs further validation and is tempered by the lack of an untreated control group that is similarly exposed to low temperature, our results appear to be in accordance with previous reports. For instance, the low level of carbon dioxide production in both cultivars (≅100 mg CO_2/kg.hr) regardless of treatment (Figure 1B & E) while in low temperature storage in the present study was comparable to that reported by Abdullah and Tirtosoekotjo (1989) for untreated Chanee and Monthong fruits stored at 13ºC (102-106 mg CO_2/kg.hr). They also indicated low ethylene production levels [max. at 13ºC (µL C_2H_4 /kg.hr): Monthong, 2.4; Chanee, 7.0] similar to those observed in the present study for Monthong (Fig. 1C, max. 1.34 µL/kg.hr) and Chanee (max. 2.10 µL/kg.hr) while in low temperature storage. Variation due to treatment was negligible (p>0.05), indicating that 1-MCP and Ethephon application did not have a major effect on the basal ethylene production of these fruits while in low temperature storage. Interestingly, upon withdrawal from low temperature storage, ethylene and carbon dioxide production remarkably increased in both Ethephon- and 1-MCP-treated fruits to levels even higher than those observed in the untreated fruits that were continuously stored in ambient condition. Granny Smith apples (Jobling *et al*., 1991) and Conference pears (Knee, 1987) pre-exposed to cold temperature also exhibited earlier induction and increase of ethylene production upon transfer to ambient storage. Supportive of this, Lara and Vendrell (2003) found accumulation of the ripening related ACS (1-aminocyclopropane-1-carboxylate synthase) in the peel of Granny Smith apples while in cold exposure (1ºC), and its activation upon transfer to ambient condition (20ºC) concomitant with the activation of ACO (1-aminocyclopropane-1-carboxylate oxidase), lead to a rapid and enhanced ACC (1-aminocyclopropane-1-carboxylate) synthesis and/or conversion to ethylene. They further noted that longer cold exposure resulted in a shorter lag period needed to achieve the highest ethylene production after transferring to ambient condition that was likewise observed in the present study. In Monthong fruits, Figure 1C also shows that fruits exposed to low temperature for 15 days (1-MCP treated) exhibited peak ethylene production (4.41 µL/kg.hr) only after one day of transfer to ambient condition, while those exposed to low temperature for 8 days (Ethephon-treated) needed two days in ambient condition to reach the greatest ethylene production (4.91 µL/kg.hr). However in Chanee fruits, peak ethylene production was consistently exhibited one day after withdrawal from low temperature storage regardless of length of exposure to low temperature (Figure 1F). These results underline existence of innate

genetic differences between cultivars in response to low temperature storage as also reported in apples (Larrigaudière *et al*., 1997).

Dehiscence, a major determinant of storage life and an indicator of full ripeness in durian, is hastened by water loss and exposure to ethylene gas (Khurnpoon *et al*., 2008; Sriyook, 1990; and Tirtosoekotjo, 1990). Abdullah and Tirtosoekotjo (1990) reported that water loss of 10-20% is critical to dehiscence. Consistent with this, results of the present study show that the abscised and untreated fruits of both cultivars were the earliest to dehisce (Table 1) at a cumulative weight loss of 8-10% (Figure 1A and D). In the Ethephon- and 1-MCP-treated groups, the rate of weight loss in low temperature storage was reduced, with increased humidity of this environment. Although the 8-10% cumulative weight loss was approximated by the Ethephon-treated fruits (postharvest day 9) and even exceeded by the 1-MCP-treated fruits (postharvest day 16), none of them dehisced while in low temperature storage. When the fruits were transferred to ambient condition, rates of weight loss increased coincident with the surge in ethylene production, and followed by dehiscence. The Ethephon-treated fruits of both cultivars were still in excellent condition, having been exposed to low temperature for a shorter period of 9 days. While, the 1-MCP-treated fruits that were kept longer in low temperature storage exhibited husk discoloration symptomatic of ripening and chilling injury, with more severe manifestations in Chanee that further exacerbated upon storage in ambient condition. Consequently in Monthong, the Ethephon-treated fruits were stored for 5 more days in ambient condition before dehiscence, while the 1-MCP-treated fruits already dehisced in 3 days (Table 1). The current industry practice of transporting durian in low temperature storage appears to contribute to a longer shelf-life of the fruit, specifically Monthong. In Chanee, fruits only lasted for 3 more days in ambient condition regardless of treatment.

Interestingly, consistent dehiscence patterns with reference to the climacteric were observed in each cultivar. In Monthong, abscised and untreated fruits dehisced at the height of the climacteric, while both the Ethephon- and 1-MCP-treated fruits dehisced after the climacteric (Figure 1B and C). In Chanee, although dehiscence was consistently observed after the climacteric, the abscised and untreated fruits took only one day from the climacteric to dehisce, while the Ethephon- and 1-MCP-treated fruits needed two days (Figure 1E and F). These observations show that ethylene exposure, rather than weight loss, exert a major influence in the synergism between these two factors for dehiscence. Moreover, Khurnpoon *et al*. (2008) demonstrated that dehiscence in durian is mediated by polygalacturonase, an ethylene-regulated enzyme. Reduced activity of this enzyme in the pulp has been associated with the retention of firmness of durian fruits stored in 12ºC (Imsabai *et al*., 2002). The role of polygalacturonase in the husk on dehiscence, and its possible regulation by ethylene and temperature could not be totally disregarded and needs to be further elucidated.

The apparent lack of efficacy of 1-MCP in the present study requires further investigation. The climacteric has not been suppressed in the 1-MCP-treated fruits. Consequently, these fruits exhibited the ripening-associated changes including reduction of pulp firmness that was comparable among all treatment groups upon dehiscence (p>0.05, Figure 2). However, a wide variation in firmness symptomatic of uneven or delayed fruit ripening was noted in the replicate fruits of 1-MCP-treated Chanee at dehiscence (Figure 2 Chanee) that attenuated 3 days post-dehiscence. This likely suggests a greater sensitivity of Chanee to the ethylene antagonist. Blankenship and Dole (2003) also noted cases of impaired softening despite unaltered climacteric ethylene production in some fruits and specific fruit cultivars treated with 1-MCP. All of these suggest that the use of 1-MCP as a postharvest treatment to prolong the storage life of durian has a strong potential, but needs to be further characterized (i.e. cultivar-specific response in terms of ACS and ACO synthesis and activation) and optimized (i.e. concentration, maturity stage of fruit at treatment, low temperature/ambient post treatment storage, etc.).

Changes in the volatile composition of durian

The unique flavor and odor of durian is described to be a combination of offensive sulfury onion-like and delicately fruity notes. Of the 137 volatile constituents reported in durian to date, the sulfur-containing compounds and esters listed in Table 2 were consistently cited as having a major impact on the characteristic aroma and flavor of the fresh pulp (Baldry *et al*., 1972; Moser *et al*., 1980; Wong and Tie, 1995; Weenen *et al*., 1996; Chin *et al*., 2007; Voon *et al*., 2007). Nanthachai (1994) cited that the ripened odor of durian is already detectable a day before the climacteric. In the present study, pulp samples for volatile analysis were collected with reference to dehiscence, which did not necessarily coincide with the climacteric. Esters were already detected in the aroma volatiles of abscised and 75-85% mature durian fruits, while only the former were detected of some sulfur compounds (i.e. diethyl disulfide and the two isomers of 3,5-dimethyl,1,2,4-

Table 2. Details of representative aroma and flavor compounds for quantitative analysis in durian pulp (Odour description by Burdock, 2002; Weenen *et al*., 1996)

Compound	CAS No.	Odor Description
Sulfur Compounds		
1-Propanethiol	107-03-9	Cabbage, sweet onion-like
Diethyl disulfide	110-81-6	Sulfury, roasty, cabbage-like
3,5-dimethyl, 1,2,4-trithiolane	23654-92-4	Sulfury, heavy, cocoa
Esters		
Ethyl propanoate	105-37-3	Reminiscent of rum and pineapple
Ethyl, 2-methyl butanoate	53956-13-1	Powerful green, fruity apple-like
Ethyl hexanoate	123-66-0	Fruity, ester-like
Ethyl octanoate	106-32-1	Fruity, floral, wine, brandy

CAS: Chemical Abstracts Services

trithiolane) one day after harvest (data not shown). Apparently, the sulfur volatiles were only produced after autocatalytic ethylene production, as they were not found in the 75-85% mature fruits a day after harvest. Using the compounds in Table 2, we have shown that the different treatments effected cultivar-specific variations on the sulfur-containing volatiles and esters of dehiscent fruits. Chin *et al*. (2008) also used these compounds to quantitatively demonstrate the effect of processing on the flavor and aroma of durian.

Upon dehiscence, a total of 7 sulfur-containing compounds and 15 esters were extracted from the fresh pulp by HS-SPME at 30ºC, with more volatiles found in Chanee than in Monthong. This is consistent with the report of Siriphanich (1994) that Monthong has a milder aroma compared to Chanee. Esters appear to be the predominant volatile aroma compound in Monthong and Chanee durian (Table 2, Figure 3) at the extraction conditions used in this study. Voon *et al*. (2007) and Wong and Tie (1995) reported that the volatile constituents of the Malaysian cultivars D2, No. 15, No. 28 and No. 74 were also predominated by esters. The esters propyl propanoate, propyl 2-methyl propanoate, propyl butanoate, and methyl octanoate were detected in Chanee, but not in Monthong. The major esters common in both cultivars were predominated by ethyl 2-methyl butanoate that was also found in highest concentration in Malaysian durian cultivars (Baldry *et al*., 1972; Wong and Tie, 1995; Jiang *et al*., 1998; Voon *et al*., 2007; Chin *et al*., 2007). The other major esters include ethyl octanoate, ethyl propanoate, and ethyl hexanoate, which were also reported by Jiang *et al*. (1998).

Sulfur compounds mainly contribute to the offensive aroma of durian. Five sulfur-containing compounds were detected in both cultivars that had also been reported previously (Wong and Tie, 1995; Jiang *et al*., 1998; Voon *et al*., 2007). These included 1-propanethiol, methyl ethyl disulfide, diethyl disulfide, and the two isomers of 3,5-dimethyl, 1,2,4-

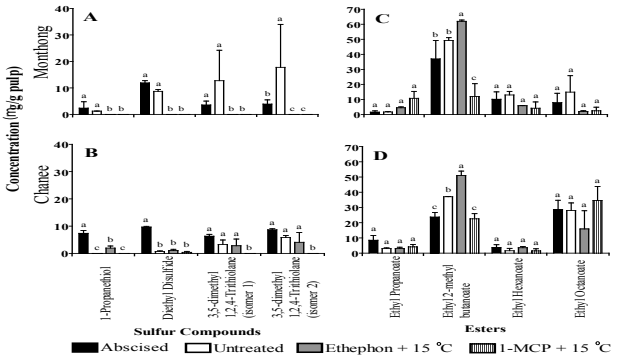

Figure 3. Concentration of representative volatile compounds upon dehiscence of Chanee and Monthong durian in the different treatment groups. Results were means (µg/g fresh pulp) ± SE of three replicate fruits extracted by HS-SPME coupled with GC-MS analysis.

trithiolane. On the other hand, the sulfur-containing volatiles diethyl trisulfide and ethanethiol were found in Chanee, but not in Monthong. Several groups reported the presence of hydrogen sulfide that was not detected in this study (Baldry *et al*., 1972; Moser *et al*., 1980; Jiang *et al*., 1998). Our results were in accordance with those of other investigators that also did not detect hydrogen sulfide (Wong and Tie, 1995; Chin *et al*., 2007; Voon *et al*., 2007).

The effect of maturity on the volatile profile of the pulp is apparently more striking in Chanee than in Monthong. In Chanee, 17 volatile compounds were found in abscised (100% mature) fruits but only 13 were detected in the untreated fruits (75-85% mature), with the difference mainly attributed to the ester compounds (Table 3). In terms of concentration, the sulfur-containing volatiles 1-propanethiol and diethyl disulfide were significantly diminished in the untreated fruits (Figure 3B). These compounds usually have a low odor threshold that makes their presence offensive even in very low concentrations (Belitz *et al*., 2009). Diethyl disulfide, for example, has an odor threshold of 0.0043 µg/g (in water). In the present study, diethyl disulfide was detected at 10 µg/g in the abscised Chanee fruits, but was decreased by 10 folds in the untreated fruits (Figure 3B). In contrast, diethyl disulfide level was comparable (10 µg/g pulp, $p>0.05$) between abscised and untreated Monthong (Fig. 3A). Chin *et al*. (2008) reported 40 µg/g diethyl disulfide in Malaysian durian. Methyl ethyl disulfide and methyl 2-methyl butanoate, were also present in the abscised fruits and not in the untreated fruits of Monthong. All of these demonstrate that naturally abscised fruits (100% mature) produce a fuller aroma upon ripening. Apparently in Monthong, the 75-85% mature fruits (untreated) have the capacity to produce the major aroma compounds in levels at par with the 100% mature fruits upon full ripeness (Figure 3A and C).

The production of sulfur-containing volatiles

Table 3. Identification of volatile compounds from the fresh pulp of dehiscent durian fruits subjected to different treatments using HS-SPME coupled to GC-MS. Results are means ± SE of three replicate fruits.

Volatile Compounds	RT	Monthong				Chanee			
		Abscised	Untreated	Ethephon od/pd	1-MCP od/pd	Abscised	Untreated	Ethephon od/pd	1-MCP od/pd
Sulfur Containing Compounds									
ethanethiol	0.7	–	–	–/–	–/–	+	–	+/+	–/–
1-propanethiol	1.1	+	+	–/+	–/+	+	–	+/+	–/–
methyl ethyl disulfide	4.9	+	–	–/–	–/–	–	–	+/–	–/–
diethyl disulfide	8.1	+	+	–/+	–/+	+	+	+/+	+/+
3,5-dimethyl, 1,2,4-Trithiolane (isomer 1)	19.0	+	+	–/+	–/+	+	+	+/+	–/–
3,5-dimethyl, 1,2,4-Trithiolane (isomer 2)	19.3	+	+	–/+	–/+	+	+	+/+	–/–
diethyl trisulfide	19.4	–	–	–/–	–/–	–	+	–/–	–/–
Total		5	4	0/4	0/4	5	4	6/5	1/1
Esters									
ethyl propanoate	1.9	+	+	+/+	+/+	+	+	+/+	+/+
ethyl 2-methyl propanoate	2.3	–	–	–/–	+/–	+	–	+/+	+/+
methyl 2-methyl butanoate	2.9	+	–	–/–	+/–	+	–	+/–	+/–
ethyl butanoate	3.4	+	+	+/+	+/+	+	+	+/+	+/+
propyl propanoate	3.5	–	–	–/–	–/–	+	–	+/–	+/–
ethyl 2-methyl butanoate	4.8	+	+	+/+	+/+	+	+	+/+	+/+
propyl 2-methyl propanoate	5.2	–	–	–/–	–/–	–	–	+/–	–/–
propyl butanoate	7.1	–	–	–/–	–/–	+	–	+/–	–/–
propyl 2-methyl butanoate	10.4	+	+	+/+	+/+	+	+	+/+	+/+
ethyl hexanoate	14.0	+	+	+/+	+/+	+	+	+/+	+/+
propyl hexanoate	18.2	+	+	+/–	–/–	+	+	+/+	+/+
ethyl heptanoate	18.3	+	+	+/+	–/–	+	+	+/+	–/+
methyl octanoate	19.2	–	–	–/–	–/–	–	–	–/–	+/–
ethyl octanoate	21.7	+	+	+/+	+/+	+	+	+/+	+/+
ethyl decanoate	27.3	–	+	–/–	–/–	–	+	–/–	–/–
Total		9	9	8/7	8/6	12	9	13/9	11/9

RT: retention time on HP-5MS capillary column
od: on dehiscence
pd: 3 days post dehiscence
Compounds were identified tentatively by comparison of mass spectrum with the NIST library spectrum (over 90% similarity).

appeared to be more susceptible to alterations mediated by postharvest treatments than esters. In Monthong, no sulfur-containing volatile was detected in Ethephon- and 1-MCP-treated fruits upon dehiscence (Table 3, Figure 3A), with these groups both subjected to low temperature storage. However, their capacity to produce these sulfury constituents was recovered 3 days after dehiscence (Table 2, Figure 3). With further validation, this observed delay may implicate a critical role and potential use of manipulating storage temperature in controlling the level of sulfur-containing compounds in durian, specifically Monthong. In contrast, Chanee fruits rather demonstrated responsiveness to the chemical treatments. Application of 1-MCP abolished the capacity of Chanee fruits to produce the major sulfur-containing volatiles, except diethyl disulfide (Figure 3B). Keeping these fruits for 3 days in ambient condition after dehiscence did not recover the capacity of these fruits to produce the sulfury constituents (Table 3). On the other hand, Ethephon application in Chanee enhanced the capacity of these fruits to produce all the major sulfur-containing volatiles upon dehiscence, including 1-propanethiol that was not detected in untreated fruits (Figure 3B). These compounds were stable even after 3 days of storage post-dehiscence in ambient condition (Table 3). Voon *et al.* (2007) reported that the sulfur compounds, specifically diethyl disulfide and methyl ethyl disulfide, in the pulp of durian kept in 4°C were stable up to 42 days of storage, as well as the two isomers of 3,5-dimethyl,1,2,4-trithiolane. In the present study, only methyl ethyl disulfide was lost in storage.

All the major ester compounds were detected in all the treatment groups upon dehiscence in almost comparable concentrations (Fig. 3C and D). Interestingly, ethyl 2-methyl butanoate appears to be increased by Ethephon treatment in both cultivars, while in Monthong, 1-MCP treatment significantly decreased the concentration of this ester. (Defilippi *et al*., 2005) also reported in Greensleeves apple that the esters of 2-methyl butanoate are sensitive to ethylene regulation. However, esters are more likely lost in storage. Table 3 shows that the number of esters decreased in both the Ethephon- and 1-MCP-treated fruits, with methyl 2-methyl butanoate consistently lost in these groups, after 3 days of storage post-dehiscence, as also reported by Voon *et al*. (2007). The loss of esters during storage is due to hydrolysis to their corresponding alcohols and acids, which is an important indication of loss in freshness and senescence of fruits.

The observations in the present study serve as impetus for a more thorough investigation on the production of volatiles in durian. Although studies on the constituents of durian's intriguing aroma abound, information on the biosynthetic pathways, accumulation of the primary substrates and final products, and their regulation in the fruit during ripening has not been given much attention. Furthermore, research on aroma and flavor volatiles in fruits, in general, has been more focused on esters and less on the production of the sulfur-containing aroma compounds. Many of the sulfury aroma constituents like thiols, thioethers, tri- and disulfides come from monosaccharides and the amino acids cysteine, cystine and methionine (Belitz *et al*., 2009). Interestingly, the production of esters also involves some amino acids as precursors like the isoleucine-derived

2-methyl butanoates (Defilippi *et al*., 2005). This suggests that the two important aroma components of durian (i.e. esters and sulfur-containing compounds) may both be regulated upstream in the production of the amino acid precursors. However, published information on the accumulation of these primary substrates, the related enzymes and the regulation of these processes in durian, and fruits in general, has been menial (Defilippi *et al*., 2005). Moreover, it is known that the final events in the production of some sulfur-containing compounds and esters are differentially regulated, with the former involving a thermochemical reaction and the latter mediated enzymatically (Belitz *et al*., 2009). The cultivar-specific differences found in the aroma profile of the present study in response to low temperature storage and the chemical treatments may likely be explained by characterizing these biochemical events in durian. The authors endeavor to pursue future research along this direction.

Conclusion

Existing industry practices for durian produce cultivar-specific variations on the aroma profile of durian. Specifically, the offensive sulfury note of durian is subject to control by conditions at harvest and postharvest. While production of the sulfur compounds in Monthong fruits are effectively delayed by low temperature exposure, those of the Chanee fruits appear to respond to the postharvest application of chemical ethylene regulators. The prospect of using 1-MCP to prolong the storage life of and control sulfur-containing volatile production in durian is promising, and needs to be further optimized. This study provides impetus for further research to serve as basis in formulating industry guide for the production and successful marketing of durian at a quality that is responsive of the needs of the target market. Control of the sulfur compounds in durian is not only of interest from a product quality perspective, but may also have an implication on food safety. The International Organization for Standardization (ISO, 2005) defines food safety as "the concept that food will not cause harm to the consumer when it is prepared and/or eaten according to its intended use". While information on food-borne hazards abound, the concept of "intended use" has not been given much attention. In the present study, we have shown information that conditions at harvest and postharvest influence the levels of sulfur-containing compounds that may mediate risky interactions with other components of the diet.

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