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## Review Article

## Volatile sulfur compounds in tropical fruits

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## ARTICLE INFO

## Article history:

Received 2 November 2017

Received in revised form

16 January 2018

Accepted 22 January 2018

Available online 16 February 2018

## Keywords:

Tropical fruits

Volatile sulfur compounds

Extraction methods

## ABSTRACT

Global production and demand for tropical fruits continues to grow each year as consumers are enticed by the exotic flavors and potential health benefits that these fruits possess. Volatile sulfur compounds (VSCs) are often responsible for the juicy, fresh aroma of tropical fruits. This poses a challenge for analytical chemists to identify these compounds as most often VSCs are found at low concentrations in most tropical fruits. The aim of this review is to discuss the extraction methods, enrichment techniques, and instrumentation utilized to identify and quantify VSCs in natural products. This will be followed by a discussion of the VSCs reported in tropical and subtropical fruits, with particular attention to the odor and taste attributes of each compound. Finally, the biogenesis and enzymatic formation of specific VSCs in tropical fruits will be highlighted along with the contribution each possesses to the aroma of their respective fruit.

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## 1. Introduction

Tropical fruits are a significant source of the total fruit intake around the world [1]. Consumers are seeking new taste experiences from exotic fruits, both for their tropical flavors and potential health benefits. The demand for these fruits is at an all-time high as they are now more accessible to consumers that live considerable distances from the regions where the fruits are cultivated. In the scientific literature, the major volatile constituents of many of the popular tropical fruits have been identified and the biogenesis of these compounds has been defined. Less understood are the trace molecules, many of which are equally important to the odor and taste profile of a specific tropical fruit. One chemical class of

compounds that falls into this category includes volatile sulfur compounds (VSCs). A recent review categorized the abundance of the key food odorants (KFOs) in natural products into three main groups: generalists, intermediaries, or individualists [2]. Many of these KFOs are VSCs. For example, 3-(methylthio)-propanal (methional) is found in 54% of the KFOs studied in the literature and listed as a generalist in natural products. Methional can be formed through the thermal or enzymatic breakdown of L-methionine and is commonly perceived by gas chromatography-olfactometry (GC-O) [3]. The next class of VSCs in foods is called intermediaries, like furfurylthiol, which are found in 15% of KFOs. Furfurylthiol, formed from carbohydrate and amino acid (AA) precursors [4], is a characteristic odorant of brewed

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E-mail address: [robert.cannon@iff.com](mailto:robert.cannon@iff.com) (R.J. Cannon).<https://doi.org/10.1016/j.jfda.2018.01.014>1021-9498/Copyright © 2018, Food and Drug Administration, Taiwan. Published by Elsevier Taiwan LLC. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

coffee [5]. Finally, VSCs can also be classified as individualists, which comprise less than 5% of the KFOs. An example would be 1-p-menthene-8-thiol, formed from AA or hydrogen sulfide and isoprenoid precursors [6]. This compound is found in only 0.4% of KFOs and is characteristic to the aroma of grapefruit juice [7] and will be discussed in more detail in later sections.

VSCs provide the juicy, fresh, authentic aroma to many varieties of tropical fruits. However, there are many challenges to identifying these compounds in natural products. The chemistry of VSCs is not always well understood as much of the literature only describes the major constituents that comprise a natural product. There is also the potential instability of VSCs, particularly thiol compounds, to oxidation and disulfide formation, as well as the adsorption to reaction and extraction vessels. Another factor is the low concentration at which VSCs occur in foods. VSCs in citrus fruits, for example, are rarely reported in the literature, mainly because the VSCs are found at extremely low concentrations and are concealed by higher concentrations of monoterpenes and sesquiterpenes. Therefore, large extractions of juice or peel are usually required, along with multiple analytical techniques and instrumentation to enrich and separate different chemical classes of compounds. Yet there still is no guarantee that the VSCs will be identified, especially when they are found in the  $\mu\text{g/L}$  and  $\text{ng/L}$  ranges. At these levels, VSCs may fall out of the detection limits of gas chromatography-mass spectrometry (GC–MS). One way to increase the level of VSCs is through thermally processing. This would most likely alter the aroma and taste of the fruit, thus changing the original, fresh profile for which the fruit is most likely being studied.

This review aims to discuss the extraction and enrichment techniques, along with the instrumentation available, to identify and quantify VSCs in natural products. This will be followed by a discussion of the VSCs reported in tropical and subtropical fruits, with particular attention to the odor/taste attributes of each compound and the specific contribution each possess to their respective fruit. Also, additional discussion will be shared on the biogenesis and enzymatic formation of these compounds. A fruit with at least 10 VSCs reported in the literature was considered a major topic for this review. Fruits with less than 10 VSCs reported were combined under the miscellaneous section at the end of the discussion.

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## 2. Extraction

Extraction and enrichments methods to identify and quantify VSCs are widely discussed in the literature [8]. One must be critical of these methods when it comes to the analysis of natural products. In terms of a known flavor formulation with compounds at known concentrations, it becomes significantly easier to measure how well a specific extraction process recovers each analyte. But for natural products, the matrix is more complex and the compounds targeted for extraction are many times unknown and vary in terms of molecular weight, solubility, and polarity; therefore making it difficult to measure the extraction efficiency and effectiveness. Thus, the extraction of a fresh fruit must be

carefully analyzed to fully discern whether the volatile compounds of the fruit have been extracted properly. One easy way to do this from a liquid–liquid extraction (LLE) is to make sure the extract produced has a very similar odor profile to the fruit, which can simply be done by dipping a paper blotter in the extract. However, this is more difficult when the flavor extraction is something other than LLE, for example solid phase micro-extraction (SPME) and stir bar sorptive extraction [9].

The fresh, unique flavor of tropical fruits is mainly consumed raw. Therefore, in order to identify the compounds that are responsible for each fruit's flavor profile, the extraction process should limit thermal processing as much as possible. Many of the isolation and concentration techniques require varying levels of thermal processing and must be taken into account in the final analysis to determine if any artifacts have formed [10,11]. The current industry standard to isolate and enrich the volatile constituents from a natural product is solvent assisted flavor evaporation (SAFE) [12]. This method is preferred as it limits thermal artifacts compared to other distillation techniques, including Likens Nickerson distillation, more commonly known as steam distillation extraction (SDE). SAFE can isolate volatile compounds with very little discrimination, including polar, less volatile, and unstable constituents that could be important to many flavor types. Using additional distillation (Vigreux column) and microdistillation (Bemelmans/Kuderna Danish column) techniques [11], SAFE extracts can be further reduced to increase the analyte concentration within the solvent. When you dip a blotter into a SAFE extract, the odor closely matches the natural product being studied, which is the critical factor to identifying the key odorants that are representative of the flavor.

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## 3. Enrichment

Many of the key odorants to the aroma of tropical fruit are found at particularly low concentrations. These odorants can be identified and characterized by GC-O but may be below the detection limits of GC–MS. There are several techniques to further enrich these odorants during the extraction process. Fractionation has been a common practice whereby the extract is added to a column (i.e. silica gel), and the constituents of the extract are separated and enriched using a gradient of different polarity solvents.

Many of the VSCs found in tropical fruits are thiol compounds in the  $\mu\text{g/L}$  and  $\text{ng/L}$  ranges. Techniques for thiol enrichment have been extensively explored over the last 15–20 years, especially in the study of wines. The most common technique found in the literature describes low level thiol compounds is LLE followed by the reversible complex of thiols to p-hydroxymercuribenzoic acid [13] or to chloromethyl polystyrene resins [14]. These bound thiols are then released by adding another thiol like L-cysteine or dithiothreitol, which can be subsequently removed from the extract by SAFE. More recently, researchers have experimented with chemical derivatization of thiol compounds using compounds such as 2,3,4,5,6-pentafluorobenzyl bromide [15,16] and 4,4'-dithiodipyridine [17].

#### 4. Instrumentation

There are many instruments available to identify VSCs in tropical fruits. Similarly to the extraction and enrichment steps, care must be taken when designing methods to inject VSCs from an extract or headspace trap onto an instrument. The hot injection temperatures (250 °C) of a gas chromatograph (GC) can cause thermal degradation or reactions to take place, especially for VSCs [18,19]. Therefore, cool on-column injections have become the favored technique for GC.

There are three main detectors that can selectively identify VSCs. These include pulsed flame photometric detector (PFPD), atomic emission detector (AED), and chemiluminescence sulfur detector (CLSD). A comparison of the detection limits, linearity, and specificity for each detector is shown in Table 1.

For a compound to be claimed as “nature identical” or “found in nature”, a peer reviewed article must irrefutably prove the presence of that peak in an extract from a minimum of two orthogonal columns using GC–MS, along with the synthesized or purchased authentic standard. The power and sensitivity of GC–MS has increased greatly over the last couple of decades, leading to new instruments, including multidimensional GC–MS (MDGC-MS), two dimensional GC–MS (GCxGC-MS), and (quadrupole) time of flight instruments, all of which possess high resolution power to identify compounds at trace levels [20].

Arguably the most important instrumental technique for the study of volatile compounds in natural products is GC-O. Even with the recent advances to the sensitivity and resolving power of the instruments described above, the human nose is still more sensitive and irreplaceable to the characterization of natural products. Using GC-O with a sulfur specific detector can further enhance the identification and understanding of VSCs [21]. Important techniques have been developed that utilize GC-O to help identify the key odorants, including Charm analysis [22] and Aroma Extract Dilution Analysis (AEDA) [23]. By AEDA, an extract is run by GC-O and stepwise diluted by a factor of two or three until no odorants are detected. Each odorant is assigned a flavor dilution (FD) factor based on these dilutions. This is a way of numerically representing the strength of the odor. For example, a calculation can begin with the formula,  $3^n$ , where 3 is the dilution factor (3-fold) and n is the last dilution the odor was smelled. A compound smelled up to the fourth dilution would have FD of  $3^4$  or 81.

**Table 1 – A comparison of three sulfur specific detectors: AED, CLSD, and PFPD (unpublished data).**

Detector	MDL <sup>a</sup> (ppm)	Linearity <sup>b</sup>	Specificity
AED	1	5	1.00E + 06
CLSD	0.1	5	1.00E + 08
PFPD	0.05	2.5	1.00E + 07

<sup>a</sup> MDL – minimum detectable limit of sulfur.

<sup>b</sup> In orders of magnitude.

#### 5. Quantitation

Another important aspect to understanding the value of VSCs to a tropical fruit is to measure their concentration in the product. A simple, semi-quantitative approach is using an internal standard at a known concentration during the extraction process. There can be significant losses of certain compounds during the extraction process, which is focused on isolating and enriching a wide range of either volatile compounds, non-volatile compounds, or both from a food matrix. To correct for these losses and better understand extraction recoveries, a more accurate approach is through stable isotope dilution analysis (SIDA) [24]. For example, a preliminary extraction using an internal standard can be added to the sample to identify the key odorants by GC-O and AEDA. The internal standard will provide semi-quantitative data for the concentration of each of the key odorants. Next, a second extraction of the same sample is made with the respective synthesized (or purchased) deuterated or carbon-13 labeled compounds which measured high FD factors by AEDA. These deuterated compounds are added to the food product at the approximate level their respective natural odorant is found in the food based on the preliminary extraction. Then the same extraction is applied to accurately quantify those specific compounds with the deuterated derivative standards. These standards should experience the same losses during extraction and help to provide accurate quantitation of the key odorants in the food.

Depending on the goal of the study, there are references for odor and taste detection thresholds (in air, water, or other media) for the most common flavor compounds [25,26]. This data, along with the concentration of the odorant in the tropical fruit, can help calculate a compound's odor activity value (OAV) [27]. AEDA helps determine which compounds have the highest contribution or potency to the aroma profile of the natural product. These key odorants, along with their concentrations using SIDA and OAVs, provide valuable insights into recombinatory and omission testing studies. This is a model approach defined as molecular sensory science or sensomics [28].

#### 6. Generation of VSCs

The biogenesis of fruit volatiles has drawn more attention lately [29], especially as the set of key odorants and olfactive space in natural products becomes more understood and defined [2]. Volatile compounds can be formed through primary enzymatic processes during intact fruit ripening or through secondary enzymatic processes when the fruit is cut or homogenized for consumption. The ripening of fruit and the increase of volatile odorants can be driven by many factors, including increased production of ethylene and enzyme activity, as well as the permeability of cell membranes. These multistep enzymatic reactions involve many classes of compounds including lipids, polysaccharides, proteins, and lignins. Many of the important precursors of VSCs in tropical fruits have been identified and the mechanisms have been

either postulated or revealed. When applicable, the biogenesis of the VSCs in each of the tropical fruit sections will be discussed.

## 7. Durian (*Durio zibethinus*)

Durian is a tropical fruit grown in Southeast Asia that possesses a strong sulfurous, alliaceous aroma. Described by non-Asians as the “smell of hell” [30], durian is actually one of the most popular fruits for Asian countries and considered the “king of fruits”. The first discovery of VSCs in durian was made in the early 1970s, when Baldry et al. identified seven low molecular weight sulfurs, including hydrogen sulfide, methanethiol, ethanethiol, and propane-1-thiol, in both Singapore and Malaysian fruits from the distillate of the pulp [31]. The authors suggested these VSCs could be important to the profile of the fruit, which helped fuel future research initiatives. Additional discoveries were made by Moser et al. who studied the volatile compounds of Thai durian, using both charcoal headspace traps and SDE [32]. A total of 8 VSCs were identified, and the authors highlighted several dialkyl polysulfides which were postulated as being directly related to the content of hydrogen sulfide found in the arillus of the fruit. However, several authors argue against this hypothesis in the years to come.

Fifteen years later, Wong and Tie compared the volatile compounds from three clones of Malaysian durians by vacuum distillation of the homogenized pulp, followed by extraction of the distillate with dichloromethane (DCM) [33]. Significant differences were found for the three clones in terms of the yield and composition of the 16 identified VSCs (10 of which were identified for the first time in durian). The next study by Weenen et al. was the first to use GC-O to characterize and discuss the importance of VSCs in a DCM-pentane extract of three Indonesian fruits [34]. It must be noted that the authors in this study only used one column to identify and characterize the odorants. With a complicated, sulfur-rich extract like durian, there could be errors in the link of GC-O aroma descriptors to the GC-MS identification of a VSC. Nevertheless, six of the 17 VSCs identified produced some aroma activity by GC-O and provided some initial insight into the compounds that provided the alliaceous, sulfurous notes. For example, diethyl disulfide was described as “sulfury, cabbage, roasty” and (Z)/(E)-3,5-dimethyl-1,2,4-trithiolane as “sulfury, heavy, onion, sulfury”.

The following year Naef and Velluz analyzed Indonesian durians in detail, using fractionation to further enrich the volatile extract [35]. The authors did not enzyme deactivate the fruit upon processing. The addition of  $\text{CaCl}_2$  or another method of enzyme deactivation is usually customary to maintain the true profile of the fruit during the process of extraction. Further, the authors removed the nonvolatiles by SDE using pentane. This is a thermal process that could affect the true concentration of the VSCs as well as the possibility of artifact formation (i.e. disulfides). Nonetheless, 42 VSCs were identified, synthesized, and their aroma characterized. An example of a synthesized dialkyl polysulfide included diethyl trisulfide which the authors described as “sweet, alliaceous, typical durian” and dipropyl trisulfide described as “alliaceous, roasted, green, durian”.

Additional VSCs discoveries in durian were made in the late 1990s and into the twenty-first century specifically with the Malaysian fruit [36,37]. In 2005, Jaswir et al. compared fresh durians and dehydrated (“leather”) durian by SDE with hexane [38]. Using different methods of SPME, Nazimah et al. studied the extraction efficiency of propane-1-thiol and diethyl disulfide, along with several other VSCs, in several varieties of Malaysian fruit [39]. In 2007, Hamid et al. produced two studies on Malaysian durian. The first article was focused on understanding the flavor differences between five Malaysian cultivars using SPME [40]. Results showed major differences in the profile and relative concentrations of VSCs in each of the cultivars. The second study compared the relative concentration of 12 VSCs during the storage of one Malaysian cultivar over 42 days at 4 °C [41]. Using SPME, the authors measured a significant loss of ethanethiol, propane-1-thiol and both isomers of 3,5-dimethyl-1,2,4-trithiolane over time. Ethanethiol measured 759.9 ng/g at day 0 of storage and decreased dramatically to 45.1 ng/g by day 7 and to 0 ng/g by day 21. The other VSCs either remained at the same level or even increased, suggesting the biogenesis of these compounds during maturation. Only a couple more studies [42] were completed before 2012 when Steinhaus et al. issued additional papers that comprehensively analyzed the aroma-active volatile constituents of Thai durian [43–45]. The authors extracted the pulp with DCM and removed the non-volatiles by SAFE. In order to identify the trace, high impact odorants, the extract was split and further fractionated using two different methods: silica gel chromatography with pentane-diethyl ether and thiol enrichment using a mercurated agarose gel. Using GC-MS and GCxGC-MS with synthesized authentic standards, the authors identified the compounds linked to their aroma descriptors from GC-O. The VSCs, along with their odor description and flavor dilution (FD) factors, are displayed in Table 2.

Additional GC-O experiments by static headspace (SH-GC-O) were conducted to identify the highly volatile VSCs, which included hydrogen sulfide (rotten egg; FD = 16), methanethiol (rotten, cabbage; FD  $\geq$  32), ethanethiol (rotten, onion; FD  $\geq$  32), propane-1-thiol (rotten, durian; FD  $\geq$  32), and ethane-1,1-dithiol (sulfury, durian; FD = 16). To better understand the importance of VSCs in durian, the authors then accurately quantified the concentration of these compounds in the fruit using a sophisticated SIDA method. Due the highly volatile and labile nature of these VSCs, the thiols were derivatized using a 3-buten-2-one adduct to effectively measure the concentration in the fruit pulp. Of the four VSCs studied in this report, ethanethiol had the highest concentration in the fruit (45,400  $\mu\text{g}/\text{kg}$ ). With an odor threshold in water of 0.095  $\mu\text{g}/\text{kg}$ , ethanethiol has an OAV of 480,000, which is extremely high for reported OAVs in the literature. The calculated OAVs for the other three VSCs included methanethiol at 45,000 (conc. = 26,700  $\mu\text{g}/\text{kg}$ ; odor threshold = 0.59  $\mu\text{g}/\text{kg}$ ); propane-1-thiol at 6300 (conc. = 3070  $\mu\text{g}/\text{kg}$ ; odor threshold = 0.49  $\mu\text{g}/\text{kg}$ ); and hydrogen sulfide at 330 (conc. 3340  $\mu\text{g}/\text{kg}$ ; odor threshold = 8  $\mu\text{g}/\text{kg}$ ). Most recently, Belgis et al. studied several durian and lai (*Durio kutejensis*) varieties from Indonesia by SPME [46]. Using sensory and statistical analysis, several VSCs were correlated to the sulfury, stinky aroma.

**Table 2 – The VSCs identified from the AEDA analysis of durian (adapted from Steinhaus et al. [43]).**

VSC	Odor	FD Factor
1-(ethylthio)-ethanethiol	roasted onion	1024
1-(ethylthio)-1-(ethylthio)-ethane	sulfury, onion	512
3-methylbut-2-ene-1-thiol	skunky	256
ethane-1,1-dithiol	sulfury, durian	256
1-(methylthio)-ethanethiol	roasted onion	256
1-(ethylthio)-propane-1-thiol	roasted onion	256
1-(propylthio)-ethanethiol	roasted sesame	32
1-[[1-ethylthio)ethyl]thio]ethanethiol isomer 1	roasted onion	32
1-(methylthio)-propane-1-thiol	roasted onion	16
diethyl trisulfide	fried shallot	16
1-[[1-ethylthio)ethyl]thio]ethanethiol isomer 2	roasted onion	16
(Z)-but-2-ene-1-thiol	skunky	4
1,1-bis-(ethylthio)ethane	rubbery, burnt	4
ethyl 2-(methylthio)-acetate	sulfury, fruity	4
1-[[1-methylthio)ethyl]thio]ethanethiol isomer 1	roasted onion	4
diethyl disulfide	roasted onion	2
1,1-bis-(methylthio)-ethane	metallic	2
1-(ethylthio)-1-(methylthio)-ethane	metallic	2
3-mercaptobutanol	onion, leek	2
1-[[1-methylthio)ethyl]thio]ethanethiol isomer 2	roasted onion	2

Few references discuss the precursors and mechanisms for which VSCs form in durian. Similar to the formation of volatile compounds in cheese, there is evidence that bacteria exist in the arils of the fruit [47], which could potentially catalyze the enzymatic release of hydrogen sulfide and methanethiol from L-cysteine and L-methionine, respectively, and drive many of the 94 reported VSCs in the literature (see Table 3).

## 8. Grapefruit (*Citrus x paradisi*)

There are a wide range of citrus fruits grown in the tropic and subtropic regions of the world. Both the juice and peel of citrus fruits contain VSCs that can be characteristic to the fruit, and studies have also shown that the concentration of VSCs vary during the time of harvest, as early season fruits tend to yield higher concentrations of VSCs compared to late season fruit [48].

One popular citrus variety is grapefruit. This fruit, compared to most other citrus varieties, possesses a pronounced sulfur aroma. Early experiments on the headspace of fresh grapefruit juice led to identification and quantitation of hydrogen sulfide (1.9 µg/L) and methanethiol (0.5 µg/L) [49–51]. The formation of both these compounds is consistent with the identification of its associated precursors, as Miller & Rockland identified L-cysteine and L-glutathione in grapefruit juice [52]. One may argue that the most important discovery in terms of the characteristic sulfurous aroma of grapefruit came in 1982. Demole et al. extracted and fractionated 100 L of juice to produce enough sample for the identification of 1-p-menthene-8-thiol [7]. This compound has a powerful, grapefruit-like aroma. The authors measured the taste detection threshold of (R)-1-p-menthene-8-thiol (0.00002 µg/L) and (S)-1-p-menthene-8-thiol (0.00008 µg/L), both of which were the lowest taste thresholds recorded at the time. A second VSC, 2,8-epithio-(Z)-p-menthane, was also identified, albeit

**Table 3 – The list of durian VSCs reported in the literature.**

VSC <sup>a</sup>	Reference
(E)-3,5-dimethyl-1,2,4-trithiolane	[33,34,35,36,37,38,39,40,41,46]
(Z)-3,5-dimethyl-1,2,4-trithiolane	[33,34,35,36,37,39,40,41,46]
(Z)-but-2-ene-1-thiol	[43]
1-(ethylthio)-1-(ethylthio)-ethane	[35,36,43,44]
1-(ethylthio)-1-(ethylthio)-methane (tent)	[35]
1-(ethylthio)-1-(ethylthio)-propane	[35]
1-(ethylthio)-1-(methylthio)-ethane (tent)	[35]
1-(ethylthio)-1-(methylthio)-methane (tent)	[35]
1-(ethylthio)-1-(propylthio)-ethane (tent)	[35]
1-(ethylthio)-1-(methylthio)-ethane (tent)	[35]
1-(ethylthio)-1-(propylthio)-ethane (tent)	[35]
1-(ethylthio)-ethanethiol	[33,36,43,44]
1-(ethylthio)-propane-1-thiol	[43]
1-(methylthio)-1-(propylthio)-ethane (tent)	[35]
1-(methylthio)-1-(propylthio)-ethane (tent)	[35]
1-(methylthio)-ethanethiol	[43,44]
1-(methylthio)-propane-1-thiol	[43]
1-(propylthio)-ethanethiol	[43]
1,1-bis-(ethylthio)-ethane	[39,40,41,43,46]
1,1-bis-(methylthio)-ethane	[35,43,46]
1-[[1-(ethylthio)-ethyl]thio]ethanethiol isomer 1	[43]
1-[[1-(ethylthio)-ethyl]thio]ethanethiol isomer 2	[43]
1-[[1-(methylthio)-ethyl]thio]ethanethiol isomer 1	[43]
1-[[1-(methylthio)-ethyl]thio]ethanethiol isomer 2	[43]
1-hydroxy-2-methylthioethane	[34]
1-methylethyl propyl disulfide (tent)	[40]
2,4,6-trimethyl-1,3,5-trithiane (tent)	[33]
2-ethyl-3-(ethylthio)-butan-1-ol (2 isomers)	[35]
2-ethyl-5-methyl-1,2,4-trithiolane (tent)	[35]

(continued on next page)

Table 3 – (continued)

VSC <sup>a</sup>	Reference
2-hydroxyethyl propyl sulfide	[38]
2-isopropyl-4-methylthiazole	[34]
2-mercaptoethanol	[36]
2-methylthiophene	[36]
3-(ethylthio)-2-methylbutanol (tent)	[35]
3-(ethylthio)-butanol	[35]
3-(ethylthio)-2-methylbutanol	[35]
3-(ethylthio)-butanol	[35]
3-(methylthio)-butanol (tent)	[35]
3-(propylthio)-butanol	[35]
3-(propylthio)-butanol	[35]
3,4-dithia-2-ethylthiohexane	[34]
3,5-dimethyltetraethane	[34]
3,5-dithiaheptane (tent)	[46]
3,6-dimethyl-1,2,4,5-tetraethane	[35,38]
3-mercaptobutanol	[43]
3-mercapto-2-methylpropanol (tent)	[46]
3-methylbut-2-ene-1-thiol	[43,44]
5-isopropyl-3-(methylthio)-2-butenol	[34]
5-methyl-4-mercapto-2-hexanone	[34]
benzothiazole	[34]
butanethiol (tent)	[37]
butyl ethyl disulfide (tent)	[35]
carbon disulfide (tent)	[37]
diethyl disulfide	[31,32,33,34,35,36,37,39,40,41,42,43,46]
diethyl tetrasulfide	[32]
diethyl trisulfide	[32,33,35,39,40,41,42,43,44,46]
diethylthioether	[31]
diisopropyl disulfide (tent)	[35]
diisopropyl trisulfide (tent)	[35]
dimethyl sulfide	[42]
dimethyl disulfide (DMDS)	[36,46]
dimethyl sulfone	[34]
dimethyl trisulfide (tent)	[35]
dimethylthioether	[31]
dimethylthiophene (tent)	[36]
dipropyl disulfide (tent)	[35,36,37,39,40,41]
dipropyl trisulfide	[35,37,39,40,41]
ethane-1,1-dithiol	[43,44]
ethanethiol	[31,33,37,39,40,41,43,44,46]
ethyl 2-(methylthio)-acetate	[33,34,43]
ethyl butyl disulfide (tent)	[37]
ethyl hydrodisulfide	[32]
ethyl isopropyl trisulfide	[35]
ethyl methyl disulfide	[33,34,35,36,37,40,41,46]
ethyl methyl trisulfide	[32,35]
ethyl propyl disulfide	[32,33,35,36,37,38,39,40,41,46]
ethyl propyl trisulfide	[32,33,35,39]
ethyl vinyl disulfide (tent)	[35]
ethylene sulfide (tent)	[37]
hydrogen sulfide	[31,32,37,43,44]
isopropyl propyl trisulfide (tent)	[35]
methanethiol	[31,37,43,44]
methyl 2-(methylthio)-acetate	[34]
methyl propyl disulfide (tentative)	[33,36,39,40,41]
methyl propyl sulfide (tent)	[39,40]
propane-1-thiol	[31,33,36,37,39,40,41,43,44,46]

Table 3 – (continued)

VSC <sup>a</sup>	Reference
s-(2-methylbutyl)-ethanethioate (tent)	[37]
s-ethyl 2-methylbutanethioate	[35]
s-ethyl thioacetate	[33,34,35,37,39]
s-ethyl thiobutyrate	[34]
s-methyl thiohexanoate	[34]
s-methyl thiooctanoate	[34]
s-propyl thioacetate	[33,39]
s-propyl thiopropionate (tent)	[33]
sulfur dioxide (tent)	[37]

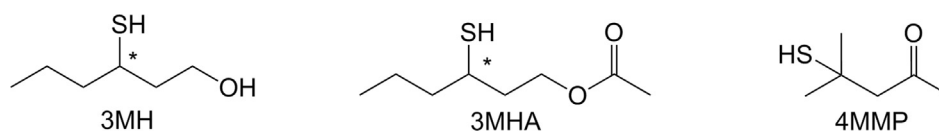
<sup>a</sup> If there is insufficient analytical data to definitively claim identification of a compound in the fruit, this compound will be considered a tentative identification and “tent” will be added to the end of the chemical name.

measured at a considerably higher taste detection threshold of 9 mg/L. This compound is most likely formed from the intramolecular cyclization of 1-p-menthene-8-thiol.

Many years later began more specific analyses to determine the role that many of the odor-active volatiles play in grapefruit juice and peel. In 1999, Buettner & Schieberle used AEDA and SH-GC-O to identify the odor-active compounds in hand-squeezed White Marsh grapefruit juice [53]. First, the fruits were enzyme deactivated with CaCl<sub>2</sub> followed by extraction with diethyl ether. The nonvolatiles were subsequently removed by high-vacuum distillation and further separated and enriched through acid/base/neutral fractionation. Three VSCs were reported in the AEDA study, including p-1-menthene-8-thiol (*grapefruit-like*; FD – 128), methional (*cooked potato*; FD – 32), and 4-mercapto-4-methylpentan-2-one (4MMP; *black currant-like*; FD – 128). Further quantitation using SIDA and reconstitution/omission testing experiments was completed two years later on the same grapefruits [54]. Results showed that 4MMP, measuring 0.8 µg/kg in the fruit with a retronasal OAV of 8,000, produced a more significant difference to the panelists when omitted from the grapefruit recombinant and provided a more authentic, true-to-fruit aroma compared to 1-p-menthene-8-thiol.

In the same year, Lin & Rouseff studied cold-pressed grapefruit peel oil from Florida [55]. The authors did not identify 1-p-menthene-8-thiol or 4MMP in the peel, instead finding a “grapefruit, flowery” aroma in 4-mercapto-4-methylpentan-2-ol and the “potato” aroma of methional. In the following year, Lin et al. studied not from concentrate (NFC), pasteurized grapefruit juice using GC-O and CLSD [56]. Three compounds were reported that were also reported in previous grapefruit research: 4MMP, methional, and p-1-menthene-8-thiol. The other two compounds, 3-mercaptohexanol (3MH) and 3-mercaptohexyl acetate (3MHA), were identified for the first time in grapefruit. Both compounds elicited a grapefruit aroma by GC-O. The structures for 4MMP, 3MH, and 3MHA are shown in Fig. 1. The possible mechanism of formation of each is discussed in detail in the passion fruit section.

Lin et al. continued to enhance our understanding of VSCs in grapefruits by studying NFC and concentrated Marsh juice by thermal processes [57]. The “meaty” 2-methylfuran-3-thiol and its dimer, bis-(2-methyl-3-furan)-disulfide, were identified in the NFC but not in the concentrate, which suggests that



**Fig. 1** – The chemical structure of 3-mercaptohexanol (3MH), 3-mercaptohexyl acetate (3MHA), and 4-mercapto-4-methylpentan-2-one (4MMP). The asterisk indicates a chiral center for which there are two possible enantiomers for each molecule.

this compound was lost during evaporation of the concentrated juice. Other VSCs found only in the NFC juice were 4MMP, 4-mercapto-4-methylpentan-2-ol, 3MH, and 3MHA. Methional was found in the thermally treated juice only, suggesting a Strecker degradation of L-methionine. Also, 1-p-menthene-8-thiol was found in the concentrated juice only, which can be explained through the reaction of increased concentrations of hydrogen sulfide and limonene. Finally, in 2010, Rouseff et al. developed a SPME method to quantitate the VSCs in the headspace of fresh and canned Marsh grapefruit juices [58]. Using PFPD, the authors also studied how the amount of oxygen affects the levels of VSCs in the juice. A total of 18 VSCs were monitored and the total concentration of VSCs was found to be higher in the canned juice compared to the fresh juice. This correlates to the degradation and secondary reactions of AAs to form different VSCs. The full list of the 17 VSCs identified in the research on grapefruit is found in Table 4.

## 9. Guava (*Psidium guajava*)

Guava is a tropical and subtropical fruit grown mainly in Latin American countries, but also harvested in certain regions of the United States, Middle East, and Asia. A significant amount of research has focused on the volatile constituents of guava, including several research articles that highlight VSCs. In

1985, Schreier and Idstein vacuum distilled the pulp of the guava fruit, followed by pentane-DCM extraction of the distillate [59]. The extract was then further fractionated on a silica gel column using a pentane-diethyl ether gradient. The authors were careful to avoid thermal reactions throughout the extraction and instrumentation process, including on-column injection of the extract. Using authentic standards for absolute identification, nine VSCs were discovered for the first time in guava including thiophenes, thiazoles, and one alkanethiol (pentane-2-thiol). In the late 1980s and early 1990s, additional VSCs were identified by Shibamoto et al. who compared pink and white guavas from the Amami islands off the southern coast of Japan [60], and Vernin et al. who studied the Egyptian fruit [61]. Later, Demole and Bassols helped clear up the misprint in Schreier's early work by also identifying pentane-2-thiol and estimated the concentration of the compound to be between 10 and 20 µg/L in the fruit [62].

An unusual discovery came in 2001, when Fernandez et al. studied yellow guavas from Indonesia [63]. Four new thiazolidine derivatives were found after the fruit was extracted with DCM under ultrasonic treatment (see Fig. 2). The ethyl compounds possessed a leek-like aroma, and the methyl compounds had notes of leek, broad bean, and fennel. The authors postulated that both thiazolidines could be formed through the biosynthesis of L-cysteine derivatives and aldehydes (i.e. acetaldehyde).

This work was followed by Mahattanatawee et al. in 2005 [64] and Clery & Hammond in 2007 [65], where both sets of authors used headspace and solvent extraction techniques to study the volatiles of guava. Each paper identified 5 VSCs, including 3MH and 3MHA. In 2008 and 2009, Steinhaus et al. completed a comprehensive study of the aroma-active constituents of pink guava fruit from Colombia [66,67]. The fruit was extracted with DCM and the nonvolatiles were removed by SAFE. A portion of the extract was washed with sodium carbonate solution to remove the acidic compounds. The resulting neutral/basic extract was split for fractionation on a silica gel column with pentane-diethyl ether, as well as thiol enrichment on a mercurated agarose gel column by affinity chromatography. The authors did AEDA on the extracts and found methional (cooked potato; FD – 256), 3MH (grapefruit; FD – 2048), and 3MHA (blackcurrant; FD – 2048) to be the important VSCs for the aroma of this guava variety. Using a cyclodextrin derivative column, Steinhaus et al. enantiomerically separated 3MH and 3MHA to identify the ratio of these enantiomers in the fruit and to measure each compound's odor threshold in air (see Table 5).

Steinhaus et al. used this data, along with accurate quantitation by SIDA, to perform reconstitution and omission

**Table 4** – The list of grapefruit VSCs reported in the literature.

VSC	Reference
1-p-menthene-8-thiol	[7,53,54,56,57,58]
2,8-epithio-(Z)-p-menthane	[7,58]
2-methylfuran-3-thiol	[57]
2-methylthiophene	[58]
3-(methylthio)-propanal (methional)	[53,55,56,57,58]
3-mercaptohexanol (3MH)	[56,57,58]
3-mercaptohexyl acetate (3MHA)	[56,57,58]
4-mercapto-4-methylpentan-2-ol	[55,57,58]
4-mercapto-4-methylpentan-2-one (4MMP)	[53,56,57,58]
bis-(2-methyl-3-furyl)-disulfide (tent)	[57,58]
carbon disulfide	[58]
dimethyl disulfide (DMDS)	[58]
dimethyl sulfide	[58]
dimethyl sulfoxide (tent)	[58]
dimethyl trisulfide	[58]
hydrogen sulfide	[49,50,58]
methanethiol	[50,58]

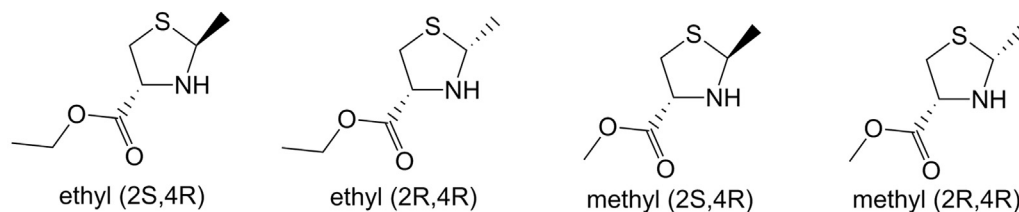


Fig. 2 – Ethyl (Z)/(E)-2-methylthiazolidine-4-(R)-carboxylate and methyl (Z)/(E)-2-methylthiazolidine-4-(R)-carboxylate found in guava fruits by Fernandez et al. [63].

Table 5 – Enantiomeric ratio and odor threshold in air of 3MH and 3MHA in pink guava fruit from Colombia measured by Steinhaus et al. [66].

	% ratio	Odor threshold in air (ng/L)
3MH		
(R)	43	0.08
(S)	57	0.07
3MHA		
(R)	42	0.10
(S)	58	0.03

testing. 3MH was measured to be 2  $\mu\text{g}/\text{kg}$  in the fruit and gave an OAV of 9300. During the omission testing, this VSC produced the largest difference in overall aroma when omitted from the reconstitute, which indicates that it is one of the most important odorants to guava. 3MHA (OAV – 570) and methional (OAV – 3.1) also showed aroma-activity in the fruit. Later, Sinuco et al. followed this study by measuring the OAV values for 3MH, 3MHA, and methional in white guava at three different stages of ripeness and pink guava at two different stages of ripeness (see Table 6) [68].

The concentration and OAV values for 3MH and 3MHA decreased considerably in the white guava as the fruit ripened from green to mature to overripe. The pink guava, however, showed an increase in 3MH and 3MHA from green to overripe. The formation of 3MH and 3MHA in tropical fruits will be discussed later in the passion fruit section, but it is worth noting that the authors were able to rule out one possible

Table 6 – The concentration and OAVs of 3MH, 3MHA, and methional at three different stages in white guava and 2 different stages of pink guava (adapted from Sinuco et al. [68]).

	3MH		3MHA		Methional	
	Conc. (ug/kg)	OAV	Conc. (ug/kg)	OAV	Conc. (ug/kg)	OAV
White						
green	16.0	270	10.0	500	0.1	<1
mature	7.8	130	9.2	460	2.3	5
overripe	1.7	30	0.4	20	0.2	1
Pink						
green	nd	–	nd	–	0.3	<1
overripe	2.2	40	2.0	100	0.1	<1

nd - not detected.

biogenesis route in guava. The authors attempted to isolate and treat the recognized precursors with  $\beta$ -lyase, but results did not produce 3MH. Instead, the authors hypothesized that unsaturated carbonyls, mainly (E)-2-hexenal could be the pathway to formation, which will be discussed further in later sections.

Over the last few years, two additional references published data on VSCs in guava. Pino and Bent identified thiazole at a concentration of 0.03 mg/kg by SDE in the Red Suprema fruit from Cuba [69]. And most recently, Plaza et al. compared fresh guava puree to that of thermally treated and dense phase carbon dioxide treatment (DPCD) [70]. The DPCD method treated the fruit puree with carbon dioxide at elevated pressures to test for its potential in retaining volatile compounds. A total of 11 VSCs were identified by SPME and relative ratios were compared between the three samples (fresh, thermal treated, DPCD). Results showed that the peak area percent for the DPCD better aligned with the area percent of the fresh puree, especially compared to that of the thermal treated data. The full list of 27 VSCs reported in guava is found in Table 7.

## 10. Lemon (*Citrus x limon*)

Native to Asia, lemons are another citrus fruit that grow in many regions of the subtropics. There are very few references of VSCs found in lemons but a recent study has revealed several VSCs that could be responsible for the aroma profile of the fresh fruit. The first discovery came in 1982 when Shaw & Wilson quantified the levels of hydrogen sulfide in the headspace of Eureka lemon juice [51]. Almost 25 years later led to the identification and quantitation of dimethyl sulfide in 4 Italian lemon juices [71]. The last report of VSCs in lemon was recently reported on Lisbon lemon peels [72]. The flavedo was zested and steeped in DCM for 24 h at 4 °C, followed by fractionation on a silica column with hexane/DCM/methanol. Two VSCs showed odor activity by AEDA: 3-methylbut-2-ene-1-thiol (*sulfurous, skunk-like*; FD – 243) and 3-mercapto-3,7-dimethyl-6-octenyl acetate (*sulfurous*; FD – 9). Recognized for its “lightstruck” aroma in beer [73], 3-methylbut-2-ene-thiol has been reported in other tropical fruits, including previously discussed durian [43]. As for 3-mercapto-3,7-dimethyl-6-octenyl acetate, there are two possible explanations for its formation. First would be the adduct of L-cysteine or L-glutathione (previously identified in lemons [52]) with neryl and geranyl acetate, both of



**Table 7 – The list of guava VSCs reported in the literature.**

VSC	Reference
1-p-menthene-8-thiol (tent)	[70]
2-ethylthiophene	[59]
2-methylfuran-3-thiol	[64,70]
2-methylthiobenzothiazole	[59]
2-methylthiophene	[59]
3-(methylthio)-propanal (methional)	[66,70]
3-mercapto-3-methylbutylformate (tent)	[64]
3-mercaptohexanol (3MH)	[64,65,66,68,70]
3-mercaptohexyl acetate (3MHA)	[65,66,70]
3-methylthiophene	[59]
4-mercapto-4-methylpentan-2-ol	[64,70]
4-mercapto-4-methylpentan-2-one (4MMP)	[70]
5-ethoxythiazole	[59]
6-mercaptohexanol	[60]
benzothiazole	[59,65]
(Z)/(E)-ethyl-2-methylthiazolidine-4-(R)-carboxylate	[63]
(Z)/(E)-methyl-2-methylthiazolidine-4-(R)-carboxylate	[63]
diisopropyl disulfide (tent)	[61]
dimethyl disulfide (DMDS)	[59,65,70]
dimethyl sulfide	[70]
dimethyl sulfone	[60]
dimethyl trisulfide	[59,65]
hydrogen sulfide	[70]
isobutyl mercaptan	[60]
methanethiol	[64,70]
pentane-2-thiol	[59,62]
thiazole	[69]

which are found at relatively higher levels in lemons compared to other citrus fruits, followed by a specific enzyme to release the thiol. The second possibility is the direct addition of hydrogen sulfide to neryl and geranyl acetate. A total of 13 VSCs were reported in this study. The full list of 15 VSCs reported in lemons is found in Table 8.

## 11. Lychee (*Litchi chinensis*)

Known for its sweet, floral flavor, lychee is a fruit native to China that is grown in many tropical and subtropical parts of the world. In 1980, Johnston et al. started the discussion of the importance of VSCs in lychee in a vacuum distilled DCM extract [74]. Using GC–MS and the Hall electrolytic conductivity detector, the authors identified benzothiazole and discussed how this compound could play a role in the sulfur aroma of the fruit. Later, Schreier and Frohlich subjected the homogenized pulp to high vacuum distillation followed by extraction with pentane-DCM and chloroform [75]. 3-(Methylthio)-1-propanol (methionol) was the lone VSC identified and the authors hypothesized the formation of this compound through the L-methionine metabolism [76]. More than 10 years later produced the first report using GC-O where the authors identified 2-acetyl-2-thiazoline as an odor-active VSC in lychee [77]. Acree and Ong homogenized the pulp with CaCl<sub>2</sub> and extracted with Freon and ethyl acetate. Using Charm analysis, 2-acetyl-2-thiazoline was described as “nutty” with a Charm value of 22,266. This compound (odor threshold in mixture – 0.5 µg/L) was found at 40.9 µg/L in the

**Table 8 – The list of lemon VSCs reported in the literature.**

VSC	Reference
2-(2-methyltetrahydrothiophen-2-yl)-ethyl acetate	[72]
2-(5-isopropyl-2-methyltetrahydrothiophen-2-yl)-ethanol isomer 1	[72]
2-(5-isopropyl-2-methyltetrahydrothiophen-2-yl)-ethanol isomer 2	[72]
2-(5-isopropyl-2-methyltetrahydrothiophen-2-yl)-ethyl acetate isomer 1	[72]
2-(5-isopropyl-2-methyltetrahydrothiophen-2-yl)-ethyl acetate isomer 2	[72]
2-(5-isopropylidene-2-methyltetrahydrothiophen-2-yl)-ethyl acetate	[72]
2-[5-(1-hydroxy-1-methylethyl)-2-methyltetrahydrothiophen-2-yl]-ethyl acetate isomer 1	[72]
2-[5-(1-hydroxy-1-methylethyl)-2-methyltetrahydrothiophen-2-yl]-ethyl acetate isomer 2	[72]
2-propionylthiophene	[72]
3-(methylthio)-propanal (methional)	[72]
3-mercapto-3,7-dimethyl-6-octenyl acetate	[72]
3-methylbut-2-ene-1-thiol	[72]
dimethyl sulfide	[71]
hydrogen sulfide	[51]
sulfur dioxide (tent)	[72]

pulp, therefore measuring an OAV of 82. The last report of VSCs in lychee came in 2007, where Rouseff et al. studied 3 cultivars from Florida [78]. A total of eight VSCs were identified using SPME, GC-O, and PFPD. The full list of the 10 VSCs reported in lychee is found in Table 9.

## 12. Mango (*Mangifera indica*)

A tropical fruit native to South America, the many varieties of mango each possess a unique flavor quality. Categorizing the volatile compounds that are responsible for a specific variety's aroma is challenging, as even the same variety grown in different regions of the same country can vary in flavor profile [79]. Tressl & Engel began the discussion of VSCs in mango by studying the Alphonso and Baladi variety [80]. The fruit was homogenized with a phosphate buffer solution and steam distilled with pentane-diethyl ether. The extract was further fractionated on a silica gel column using gradients of pentane-diethyl ether and pentane-DCM. Two VSCs were identified in

**Table 9 – The list of lychee VSCs reported in the literature.**

VSC	Reference
2,4-dithiopentane (tent)	[78]
2-acetyl-2-thiazoline	[77,78]
2-methylthiazole (tent)	[78]
3-(methylthio)-1-propanol (methionol)	[75]
3-(methylthio)-propanal (methional)	[78]
benzothiazole	[74]
diethyl disulfide (tent)	[78]
dimethyl sulfide	[78]
dimethyl trisulfide (tent)	[78]
hydrogen sulfide (tent)	[78]

the analysis of the Alphonso variety: (methylthio)-phenaldehyde and benzothiazole. Both were found at 10 µg/L in the mango but it is unclear to the reader where the methylthio group is positioned on the benzene ring of (methylthio)-phenaldehyde. Ten years later, Wong & Ong studied the kuini fruit (*Mangifera odorata*) which is closely related to the mango [81]. Applying SDE with pentane on the pulp revealed ethyl 2-(methylthio)-acetate at trace levels. Later, Yukawa et al. studied two mango varieties (Carabo and Kent) by dynamic headspace sampling [82]. The authors identified three VSCs for the first time in mango: dimethyl trisulfide; diisopropyl disulfide; isopropyl methyl disulfide. Another 12 years passed until Mahattanatawee et al. tentatively identified 2-methylfuran-3-thiol (*nutty, medicinal, cooked oily*) and 4-mercapto-4-methylpentan-2-ol (*green, grapefruit*) by GC-O from Florida-grown mangos [64].

In 2005, Pino et al. analyzed 20 cultivars from Cuba using SDE with diethyl ether [83]. There is some uncertainty in the identification of several new VSCs that were identified as there appears to be contamination or misidentified peaks. Two of the VSCs identified were diallyl disulfide and diallyl trisulfide. Up until this point, these compounds were found only in the *Allium* family, and more specifically, in garlic. There was additional confusion when the authors reported the identification of ethyl maltol and allyl cyclohexylpropionate, two compounds that have never been claimed as nature identical. Most recently, Steinhaus et al. completed a comprehensive study of the odor-active compounds in six mango cultivars from Florida [84]. The authors froze and powdered small cubes of the mango fruit using liquid nitrogen and a mill. The powder was extracted with diethyl ether and subjected to SAFE. The extract was split and fractionated on a silica gel column with pentane-diethyl ether and thiol enriched using a mercurated agarose gel. Using GCxGC-MS and GC-O, the authors completed AEDA on all six extracts and assigned flavor dilution factors for each aroma-active compound. The Haden mango variety was found to be the most sulfurous and the VSCs identified included: (E)-2-butene-1-thiol (*sulfurous*; FD – 32); 3-methylbut-2-ene-1-thiol (*sulfurous*; FD – 128); dimethyl trisulfide (*cabbage*; FD – 8); 4-mercapto-4-methylpentan-2-one (*tropical*; FD – 32); methional (*cooked potato*; FD – 512). Two years later, Steinhaus et al. further investigated the Haden mango by using SIDA and odor threshold calculations to recombine the aroma profile of the fruit [85]. Omission and sequential addition testing showed that 3-methylbut-2-ene-1-thiol (conc. – 0.0539 µg/kg; odor threshold in water – 0.00045 µg/kg; OAV – 120) and 4-methyl-4-mercaptopentan-2-one (conc. – 0.0509 µg/kg; odor threshold in water – 0.0010 µg/kg; OAV – 51) played an important role in the aroma of the Haden variety. The full list of 12 VSCs reported in mango is found in Table 10.

### 13. Muskmelon (*Cucumis melo*)

Muskmelon is a species of melon belonging to the Cucurbitaceae family. Two of the most common muskmelons include cantaloupe and honeydew, both possessing a sweet, fruity, and sulfurous aroma. It is important to note that certain melon varieties can grow outside the tropic and subtropic

**Table 10 – The list of mango VSCs reported in the literature.**

VSC	Reference
(methylthio)-phenaldehyde (tent)	[80]
2-methylfuran-3-thiol (tent)	[64]
3-(methylthio)-propanal (methional)	[84,85]
3-methylbut-2-ene-1-thiol	[84,85]
4-mercapto-4-methylpentan-2-ol (tent)	[64]
4-mercapto-4-methylpentan-2-one (4MMP)	[84,85]
benzothiazole	[80]
diisopropyl disulfide	[82]
dimethyl trisulfide	[82,84,85]
ethyl 2-(methylthio)-acetate	[81]
isopropyl methyl disulfide	[82]
(E)-but-2-ene-1-thiol	[84]

regions of the world. However, this review has not separated out the research on muskmelon fruits that may not be tropical or subtropical.

The first VSC discovery came in the late 1970s when Yabumoto et al. identified DMDS from the cantaloupe variety [86]. The authors anticipated that this finding would pave the way for future discoveries in terms of VSCs. Five years later, Buttery et al. identified ethyl 2-(methylthio)-acetate in a vacuum distillation extract of California honeydew [87]. The authors also measured the odor threshold of this compound in water to be 25 µg/L. The same compound was also confirmed in cantaloupe using similar extraction conditions by Horvat & Senter [88]. Not too long after, Homatidou et al. significantly increased our understanding of the VSCs found in cantaloupe by using MDGC-MS to separate, focus, and enrich the characteristic odorants identified by GC-O in cantaloupe [89]. A total of 8 VSCs were synthesized and confirmed as present in the extract of the fruit. An unusual discovery was the identification of 3-(methylthio)-propanenitrile. Isothiocyanates and nitrile compounds are rarely found identified in fruits and are mainly reported in the *Brassicaceae* family [90]. The formation of 3-(methylthio)-propanenitrile is based on the enzymatic hydrolysis of the thioglucoside bond of 2-(methylthio)-ethyl glucosinolate by myrosinase, which has been previously identified in cantaloupe [91]. Additional details for this specific enzymatic process will be discussed further in the papaya section.

Wyllie & Leach confirmed the presence of many of the same VSCs previously identified by Homatidou et al. and discussed how thioesters were most likely derived from L-methionine and the production of ethylene during ripening [92–94]. These thioesters were quantified above their respective odor thresholds in melon fruits and claimed as key to the odor profile of the fruit. Later, Homatidou et al. further enriched our knowledge of VSCs in melons by identifying 2-(methylthio)-ethanol among the already reported thioesters in cantaloupe [95]. Also, Wyllie et al. used AED and AEDA to identify 13 VSCs in Makdimon muskmelon, four of which were new discoveries in melon at the time [96]. S-methyl thiobutyrate, methional, 3-(methylthio)-propyl acetate, and dimethyl tetrasulfide had the highest flavor dilution factors amongst the VSCs. This study used SDE to identify the volatile constituents and any thermal processing could create thermal artifacts or affect the concentration of the aroma compounds.

Additional experiments were made in the late 1990s [97] and into early 2000s [98,99], which helped to strengthen the importance of VSCs to different varieties of muskmelon. In 2005, Aubert et al. compared liquid–liquid microextraction (LLME) and conventional LLE for the recoveries of seven VSCs [100]. Results showed that thioacetates had a higher recovery by LLME compared to LLE but thioalcohols and polar compounds in general were not as effective. The same year Senesi et al. compared the volatile composition of two cantaloupe varieties at different ripening and post-harvest stages using static headspace analysis. Differences were observed in the concentration of the VSCs from each stage of ripening and post-harvest, however no overall trends could be made with respect to the VSCs [101]. In 2012, Lin and Wang extracted the Naudin cantaloupe by solid phase extraction (SPE) using DCM and methanol [102]. Instead of SAFE, another technique called gel permeation chromatography was employed to remove the nonvolatile, high molecular weight compounds. GC-O and GC–MS led to the identification of four VSCs with ethyl 2-(methylthio)-acetate (*potato, fruity, green, vegetative, tomato, aldehyde*) being the most intense odorant.

Recent studies measured the ripening time and processing conditions on the flavor profile of melons. Using SPME, Beaulieu & Lancaster compared several varieties of fresh-cut fruit at different storage dates [103]. Later, Zakharov et al. compared three varieties of enzyme deactivated muskmelon homogenate by headspace SBSE, along with an integrated sensory quality evaluation [104]. The authors identified one cultivar, Navigator, which measured increased concentrations of ethyl 2-(methylthio)-acetate and ethyl 3-(methylthio)-propionate during ripening. These VSCs correlated to the “musky aroma” in their study and the Navigator variety was perceived as the highest in this attribute compared to the

other varieties. In the same year, Parker et al. compared three new acidic melon varieties to a standard Galia fruit by SPME and dynamic headspace [105]. Results indicated higher levels of VSCs in the new melons, especially in one variety which also had the highest levels of L-methionine, the main non-volatile precursor for these VSCs. Even more recent studies by Priyanka et al. compared the fresh Indian melon to canned puree and puree processed in retort pouches by SDE [106]. Overall the relative concentration of VSCs from the fresh fruit was higher than the processed fruit.

In 2010 and 2013, Lewinsohn et al. studied the importance of L-methionine to the formation of VSCs in melons [107,108]. In their first paper, the authors introduced exogenous L-methionine or  $\alpha$ -keto- $\gamma$ -(methylthio)-butyrate (KMBA; key intermediate of L-methionine for VSCs) into the melon fruit and measured a significant increase in the concentration of methional, ethyl 3-(methylthio)-propionate, and 3-(methylthio)-propyl acetate. The authors demonstrated that methionine transferase catabolized L-methionine to release KMBA. Using carbon-13 and deuterated labeled L-methionine, the two catabolic routes to the formation of VSCs in the melon fruit were determined. The first mechanism confirmed the proposal above whereby the structural backbone of L-methionine is retained. The second mechanism involved L-methionine- $\gamma$ -lyase which released methanethiol for secondary reactions (see Fig. 3).

The same authors identified the *CmMGL* gene that encodes a protein possessing L-methionine- $\gamma$ -lyase enzymatic activity. As the fruit ripened, an increase in the expression of this gene occurred. Finally, to help confirm the significance of this gene for the L-methionine- $\gamma$ -lyase metabolism, the authors compared two cultivars: one that had high *CmMGL* expression and one that low *CmMGL* expression. The cultivar with high

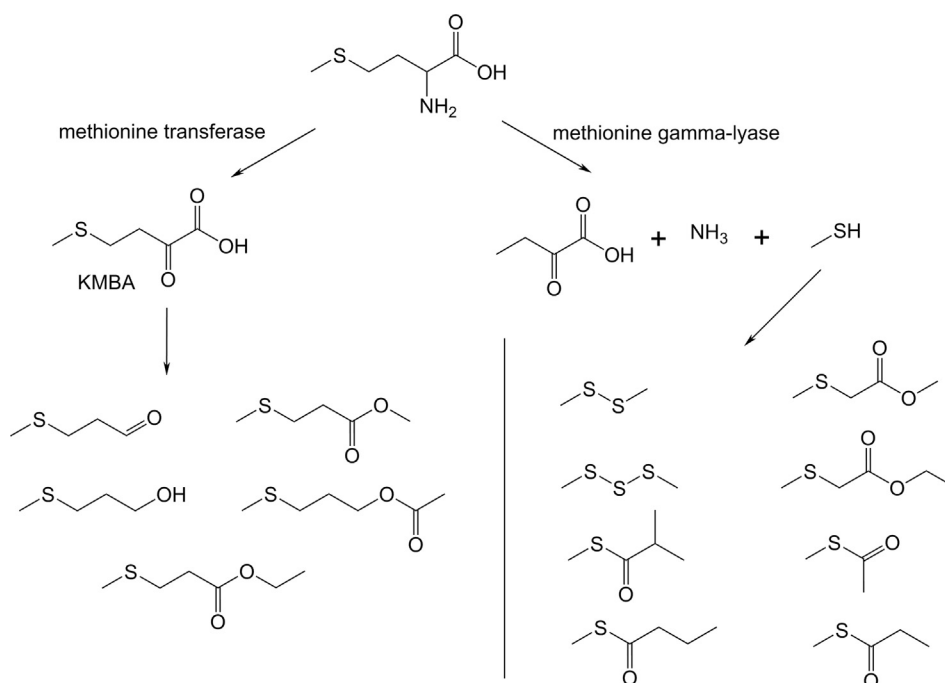


Fig. 3 – Two mechanisms for the enzymatic breakdown of L-methionine. (adapted from Lewinsohn et al. [108]).

**Table 11 – The list of muskmelon VSCs reported in the literature.**

VSC	Reference
2-(methylthio)-ethanol	[95,99,100,101,108]
2-(methylthio)-ethyl acetate	[89,92,93,95,96,100,105,108]
2-ethylhexane-1-thiol (tent)	[109]
2-methylbutane-2-thiol (tent)	[106,109]
3-(methylthio)-1-propanol (methionol)	[89,95,99,100,102,106,109]
3-(methylthio)-propanal (methional)	[96,101]
3-(methylthio)-propanenitrile	[89]
3-(methylthio)-propionic acid	[89]
3-(methylthio)-propyl acetate	[89,92,93,95,96,98,100,102,103,105,108]
dimethyl disulfide (DMDS)	[86,95,96,105,108]
dimethyl tetrasulfide (tent)	[96]
dimethyl trisulfide	[96,105,108]
ethyl 2-(methylthio)-acetate	[87,88,89,92,93,95,96,98,99,100,101,102,103,104,105,106,108,109]
ethyl 3-(methylthio)-propionate	[92,93,95,96,98,99,100,101,103,104,108,109]
methanethiol	[108]
methyl 2-(methylthio)-acetate	[89,92,93,95,96,99,100,108]
methyl 3-(methylthio)-propionate	[89,93,95,96,98,103,108]
methyl diethyl carbamodithioic acid (tent)	[98]
propyl 3-(methylthio)-acetate	[101]
s-methyl 2-methylpropanethioate	[105,108]
s-methyl 2-methylbutanethioate	[105]
s-methyl 3-methylbutanethioate (tent)	[98,103,104,105]
s-methyl thioacetate	[102,105,108]
s-methyl thiobutyrate	[96,104]
s-methyl thioethanoate	[96,98]
s-methyl thiopentanoate	[96]
s-methyl thiopropionate (tent)	[108]

levels of the CmMGL gene led to a significantly higher concentration of VSCs compare to the cultivar with low levels of the gene. Therefore, L-methionine- $\gamma$ -lyase activity appears to be the dominant pathway over L-methionine aminotransferase in this fruit.

More recently, Li et al. showed that ethylene was important to the regulation of gene expression and transferase activity for L-cysteine catabolism and the generation of several VSCs [109]. However, it is not clear from the research how L-cysteine could generate the specific VSCs identified in the report, which included methionol, ethyl 2-(methylthio)-acetate, and ethyl 3-(methylthio)-propionate. The full list of 27 VSCs reported in melon is found in Table 11.

## 14. Orange (*Citrus x sinensis*)

Similar to grapefruit, the VSCs reported in orange depend on the variety and whether research was completed on the juice or the peel. Early studies by Shaw in 1980 showed that both Valencia and Navel oranges contained hydrogen sulfide and

**Table 12 – A comparison of 2-methylfuran-3-thiol and methional under 3 processing conditions of orange juice (adapted from Naim et al. [113]).**

Compound	Fresh (ng/L)	Pasteurized (ng/L)	Stored (ng/L)
2-methylfuran-3-thiol	1.8	1.9	270
methional	550	830	11,550

methanethiol in the headspace of the juice [50]. Fifteen years later Naef et al. used continuous LLE to identify the odorants from blond and blood orange juice [110]. The extract was further fractionated on a silica gel column using pentane-diethyl ether. Diisopropyl disulfide and diisopropyl trisulfide were tentatively identified in both fruits. The authors synthesized the third VSC, S,S-ethylidene dithioacetate (*alliaceous, transpiration*), for confirmation of its presence in the blood orange fruit. This was the first report of this compound in a natural product.

In 1998, Schieberle & Hinterholzer studied Osbeck orange juice from the Mediterranean [111]. The juice was subjected to enzyme deactivation and extracted with diethyl ether. The volatiles were isolated by high vacuum distillation and further fractionated on a silica gel column using pentane-diethyl ether. The authors performed GC-O and AEDA and identified methional (*cooked potato*; FD – 64) and p-1-menthene-8-thiol (*grapefruit-like*; FD – 8), both reported for the first time in orange juice. The concentration of both odorants was beyond the detection limits of the mass spectrometer and therefore no mass spectral data was produced to support the identification. However the authors incorporated three orthogonal columns to confirm the identity of both compounds by GC-O. Two years later, Schieberle & Buettner reconfirmed these findings by studying two Osbeck varieties (Valencia and Navel) [112]. The authors quantitated methional and p-1-menthene-8-thiol by SIDA and concluded that both compounds had a low contribution to the aroma profile of the fruits according to their respective OAV values.

In that same year, Naim et al. studied the fresh, pasteurized, and stored juice (21 days at 35 °C) of Valencia and Shamuti cultivars from Israel [113]. Using SPME, 2-methylfuran-3-

**Table 13 – The list of orange VSCs reported in the literature.**

VSC	Reference
1-phenylethanethiol	[117,118,119]
2-methylfuran-3-thiol	[113,116]
3-(methylthio)-propanal (methional)	[111,112,113,116]
3-mercaptoputan-2-one (tent)	[116]
4-mercapto-4-methylpentan-2-one (4MMP; tent.)	[116]
diisopropyl disulfide (tent)	[110]
diisopropyl trisulfide (tent)	[110]
dimethyl sulfide	[50,116]
dimethyl trisulfide	[116]
hydrogen sulfide	[50]
methanethiol	[116]
p-1-menthene-8-thiol	[111,112,116]
s,s-ethylidenedithioacetate	[110]



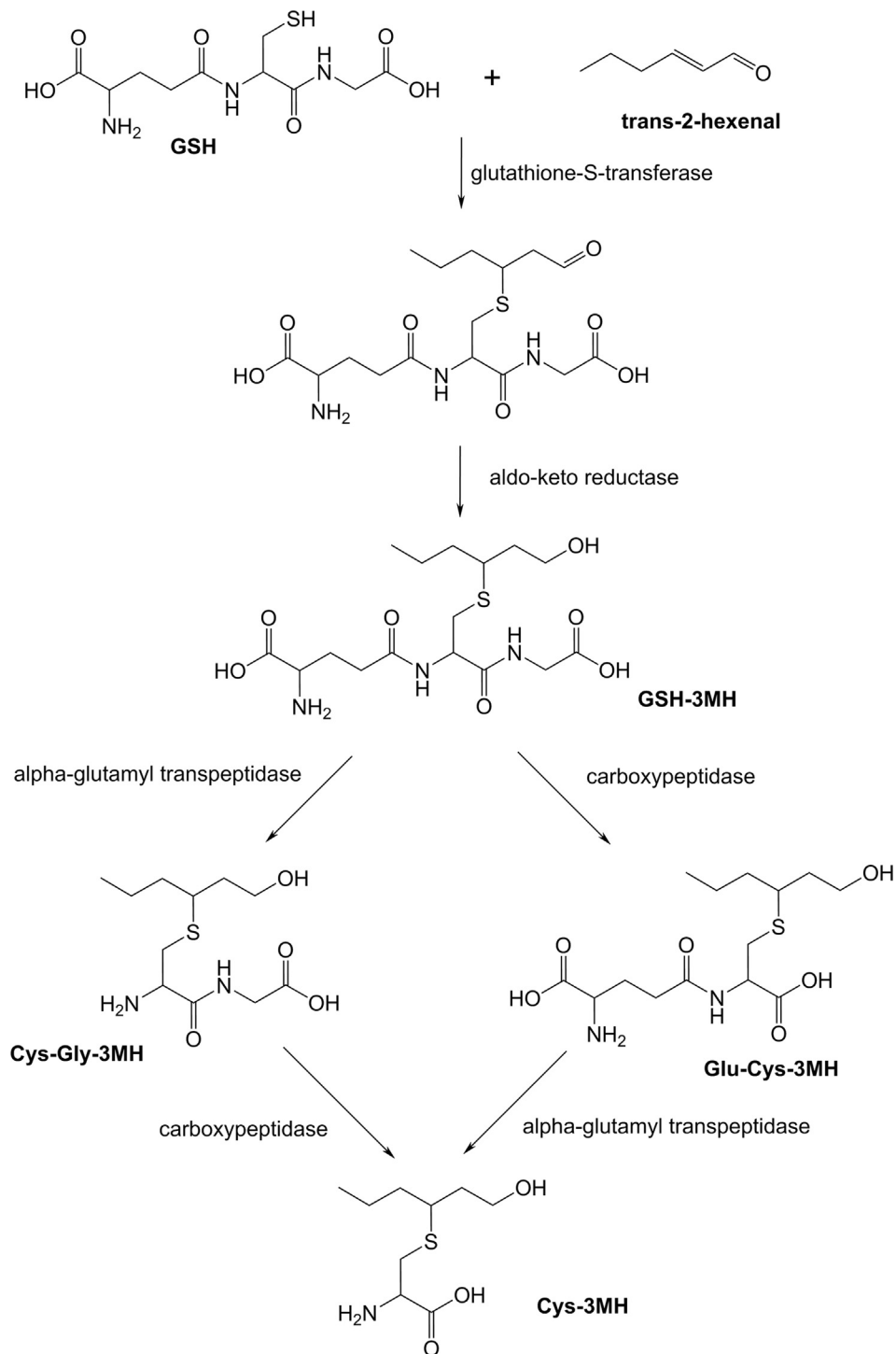


Fig. 6 – Glutathione metabolism initiated by the conjugation of GSH with (*E*)-2-hexenal (adapted from Mattivi et al. [158]).

and omission testing [118,119]. The full list of 13 VSCs reported in orange is found in Table 13.

## 15. Papaya (*Carica papaya*)

Papaya is a tropical fruit native to Latin America with a very unique flavor profile. The volatile constituents of papaya have

been studied in detail over the last 40 years with several reported VSCs. The most recognized VSC in papaya is benzyl isothiocyanate (BITC), first reported in the seeds of the fruit [120]. BITC possesses anti-cancer properties and is a character impact odorant to the fruit. In the early 1970s, Tang & Syed measured the concentration of BITC in the fruit flesh and seed [121,122], and later Nakamura et al. showed that the precursors and enzymes related to the formation of BITC are

mainly found in the seeds of the fruit [123]. As mentioned earlier in the guava section, isothiocyanates are uncommon to find in fruits. The formation of isothiocyanates in natural products can be explained by the mechanisms described in Fig. 4. Glucosinolates, derived from AAs present in papaya fruit [124,125], undergo hydrolysis by the enzyme myrosinase, also present in papaya [126], to form the intermediate thiohydroximate-O-sulphonate. This intermediate is unstable and loses a sulfate group to undergo a Lossen rearrangement to form either isothiocyanates, thiocyanates, nitrile, or epinitriles (see Fig. 4). By this mechanism, BITC is formed in high concentrations from glucotropaeolin (see Fig. 5).

In 1977, Flath & Forrey incorporated several distillation techniques to identify BITC, methyl thiocyanate, and benzothiazole in papaya [128]. Later, MacLeod & Pieris studied Sri Lanka papayas by high vacuum distillation with pentane [129]. Both GC-O and quantitative analysis led to the identification of BITC (*earthy, cress seeds*; conc. – 1.4 µg/kg) and methyl 2-(methylthio)-acetate (*American currant*; conc. – 0.2 µg/kg). Similar to the *Carica papaya* is the *Carica candamarcensis* (mountain papaya from Chile), which was studied by Schreier et al. in 1985 [130]. Using high-vacuum distillation and subsequent solvent extraction using pentane-DCM, the authors identified 6 VSCs, including three alkyl thiophenes, ethyl 3-mercaptopropionate, BITC, and 2-phenylethyl isothiocyanate [131]. The latter compound is the second isothiocyanate identified in papaya, most likely derived from the glucosinolate named gluconasturiin [132]. In the same year, Idstein & Schreier used the same analytical procedure to identify five VSCs, including methyl thiocyanate and ethyl thiocyanate [133]. Both compounds could be formed from methyl glucosinolate and ethyl glucosinolate, respectively, in the presence of a thiocyanate-forming protein [134]. Pino et al. followed more than a decade later with a study on the Maradol papaya variety from Cuba. Using SDE, eight VSCs were identified in the first paper, including BITC [135]. Later, the same authors studied BITC over four stages of ripening and found the concentration of this compound to decrease during the ripening process [136], which differed from previous studies by Tang [121]. These results were confirmed in a later study by Cordenunsi et al. who measured levels of benzyglucosinolates and BITC in the seed, fruit, and peel during ripening [137]. The authors also concluded that ethylene does not have an effect on BITC accumulation, which is important to our understanding of which fruits rely on ethylene for the biogenesis of certain volatile compounds.

More recently, Ulrich & Wijaya studied five cultivars of papaya by first homogenizing the fruit with sodium chloride (enzyme inhibition), followed by splitting the juice for SBSE and extraction using DCM [138]. Five VSCs were identified and quantitated, and GC-O results showed BITC to be odor-active in the fruit. Further GC-O studies were completed in 2014 by Pino on the Red Maradol variety using SPME and SDE with diethyl ether [139]. By SPME, GC-O identified BITC as “papaya” in aroma and was detected with the highest frequency by the panelists, demonstrating its importance to the odor of the fruit. AEDA was completed on the SDE extract and BITC had a FD factor of 1024 and an OAV of 871. The full list of 17 VSCs reported in papaya is found in Table 14.

**Table 15 – The list of passion fruit VSCs reported in the literature.**

VSC	Reference
1,1-bis-(methylthio)-2-methylpropane	[147]
2-(methylthio)-ethyl acetate	[147]
2-methylbutyl 3-(methylthio)-propionate	[147]
3-(1-acetoxy-3-hexyldithio)-hexyl acetate	[147]
3-(1-acetoxy-3-hexyldithio)-hexyl butyrate	[147]
3-(1-acetoxy-3-hexyldithio)-hexyl hexanoate	[147]
3-(1-butyryloxy-3-hexyldithio)-hexyl butyrate	[147]
3-(1-butyryloxy-3-hexyldithio)-hexyl hexanoate	[147]
3-(1-hydroxy-3-hexyldithio)-hexanol	[147]
3-(1-hydroxy-3-hexyldithio)-hexyl acetate	[147]
3-(1-hydroxy-3-hexyldithio)-hexyl butyrate	[147]
3-(methylthio)-hexanol	[141,142,144,145,147]
3-(methylthio)-hexyl acetate	[144,147]
3-(methylthio)-hexyl butyrate	[144,147]
3-(methylthio)-hexyl hexanoate	[144,147]
3-(methylthio)-propanal (methional)	[147]
3-(methylthio)-propionate	[144]
3-(methylthio)-propionic acid	[14]
3-(methylthio)-propyl acetate	[147]
3-(methylthio)-propyl butyrate	[147]
3-(methylthio)-propyl hexanoate	[147]
3-mercapto-3-methylbutanol	[157]
3-mercapto-3-methylbutyl acetate	[157]
3-mercaptohexanol (3MH)	[14,144,145,147,157]
3-mercaptohexyl acetate (3MHA)	[14,144,146,147,157]
3-mercaptohexyl butyrate	[14,144,146,147,157]
3-mercaptohexyl hexanoate	[14,144,147]
3-mercaptohexyl pentanoate	[147]
3-methylbutyl 3-(methylthio)-propionate	[147]
4-methyl-5-vinylthiazole	[140,144,147]
butyl 3-(methylthio)-propionate	[147]
(Z)-2-methyl-4-propyl-1,3-oxathiane	[141,142,143,144,146,147]
(Z)-3-hexenyl 3-(methylthio)-propionate	[147]
diethyl disulfide	[147]
diisopropyl disulfide	[147]
diisopropyl trisulfide	[147]
ethyl 2-(methylthio)-acetate	[147]
ethyl 3-(methylthio)-(Z)-2-propenoate	[147]
ethyl 3-(methylthio)-propionate	[14,141,142,143,144,146,147]
ethyl 3-(methylthio)-(E)-2-propenoate	[141,142,143,144,146,147]
ethyl 3-mercaptobutyrate	[14]
hexyl 3-(methylthio)-propionate	[147]
hexyl 3-(methylthio)-(E)-2-propenoate	[147]
isobutyl 3-(methylthio)-propionate	[147]
methyl 2-methylbutyl disulfide	[147]
methyl 3-(methylthio)-(Z)-2-propenoate	[147]
methyl 3-(methylthio)-propionate	[147]
methyl 3-(methylthio)-(E)-2-propenoate	[147]
pentyl 3-(methylthio)-propionate	[147]
propyl 3-(methylthio)-propionate	[147]
propyl 3-(methylthio)-(E)-2-propenoate	[147]
sec. butyl 3-(methylthio)-propionate	[147]
s-methyl acetothioate	[147]
(E)-2-methyl-4-propyl-1,3-oxathiane	[141,142,143,144,146,147]

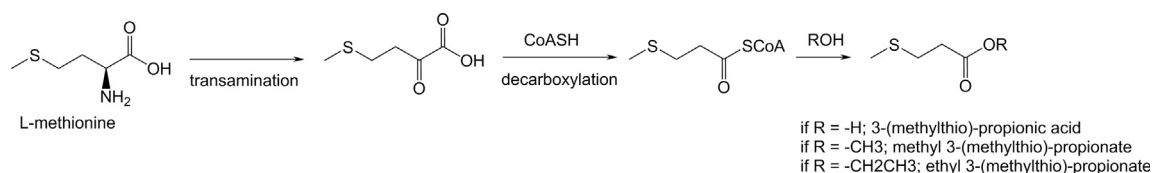
## 16. Passion fruit (*Passiflora edulis*)

Passion fruit is grown in both tropical and subtropical regions of the world and possesses a sweet, sulfurous flavor. The first VSCs reported in passion fruit were identified by Winter et al. in the 1970s, where the authors extracted over 500 kg of yellow passion fruit to identify 4-methyl-5-vinylthiazole, 3-(methylthio)-hexanol, and (Z)/(E)-2-methyl-4-propyl-1,3-oxathiane (MPO) [140,141]. The latter two compounds were further investigated for their importance to the aroma of the fruit. The enantiomers were later resolved by Heusinger & Mosandl [142] and sensory characteristics described by Mosandl et al. [143]. Based on Mosandl's report, it appears that the (2S,4R)-configuration of MPO gave the most characteristic passion fruit odor (fatty, fruity green, tropical fruits, grapefruit) and taste (fatty fruity, tropical fruits, passion fruit, guava).

The 1990s led to an even greater understanding of the scope of VSCs in passion fruit. Engel and Tressl studied yellow passion fruits by SDE using pentane-diethyl ether [144]. Twelve VSCs were identified by fractionation and PFPD on two orthogonal column phases. Two compounds identified by Engel, 3MH and 3-(methylthio)-hexanol, were also identified by Mosandl et al. who studied the enantiomeric distribution of each compound in both yellow and purple passion fruits [145]. Further enantiomeric studies were completed on MPO, 3MHA, and 3-mercaptopentyl butyrate using MDGC and a chiral

column in the second dimension [146]. The last paper of the 1990s was completed by Werkhoff et al. who completed an in-depth study of yellow passion fruits [147]. Prior to this research, 12 VSCs were identified in passion fruit. Using four different extraction techniques (vacuum headspace, dynamic headspace, SDE, vacuum SDE) [148], the authors identified 47 VSCs in total, 35 of which were new to passion fruit and 23 new to natural products. According to the authors, the extract produced from the vacuum headspace distillate provided the most typical passion fruit aroma. Each of the VSCs from this extract were synthesized and characterized. The enantiomeric distribution of 3MH, 3-(methylthio)-hexanol, and 3MHA were also studied and each favored the S-configuration. Most recently, Sakaguchi et al. focused on the identification of VSCs in passion fruit through a new thiol enrichment method [14]. The authors first used SAFE to collect a distillate of the juice, which was then added to a SPE cartridge and extracted with diethyl ether. The extract was further enriched using a chloromethyl polystyrene resin with a thiosulfinate group to selectively bind and release thiols. A total of seven VSCs were reported from this study.

Many of the mechanisms postulated and studied for the identification of VSCs in passion fruit VSCs, specifically 3MH and 3MHA, were built on the insights gained from the formation of the same VSCs in wine. In the literature, there are a few accepted mechanisms for the biogenesis of 3MH in wine. In 1998, Tominaga et al. discovered the process by



**Fig. 7** – Biosynthetic pathway of 3-(methylthio)-propionic acid, methyl 3-(methylthio)-propionate, and ethyl 3-(methylthio)-propionate from L-methionine (adapted from Wei et al. [166]).

**Table 16** – The concentration, odor threshold, and OAVs for two of the most abundant VSCs in pineapple [169].

VSC	Conc. (ug/kg)	Odor Threshold in water (ug/kg)	OAV
methyl 3-(methylthio)-propionate	596	180	3.3
ethyl 3-(methylthio)-propionate	27	7	3.9

**Table 17** – Comparison of the concentration of VSCs from different fruit juice processes adapted from Elss et al. [172].

Compound	Fresh Pineapple Juice (19 fruits) <sup>a</sup>	Pineapple Water phase/Recovery Aromas (8 products) <sup>a</sup>	Pineapple Concentrates from flavor houses (10 products) <sup>a</sup>	Commercial Single Strength Pineapple Juice (6 products) <sup>a</sup>	Commercial Pineapple Juices made from concentrate (11 products) <sup>a</sup>
methyl 2-(methylthio)-acetate	15	0.2	nd	10	nd
ethyl 2-(methylthio)-acetate	1	0.3	nd	nd	nd
methyl 3-(methylthio)-propionate	1500	112	40	550	12
ethyl 3-(methylthio)-propionate	470	109	nd	130	12
3-(methylthio)-propyl acetate	5	2.8	nd	2	nd
methionol	10	0.25	15	26	10
methional	nd	nd	90	15	7

nd - not detected.

<sup>a</sup> Mean concentration in ug/L.



**Table 18 – Comparison of the area percentage of VSCs in green and ripe pineapples adapted from Umamo et al. [173].**

VSC	Green (Area %)	Ripe (Area %)
methyl 2-(methylthio)-acetate	0.1	<0.1
ethyl 2-(methylthio)-acetate	0.1	trace
methyl 3-(methylthio)-propionate	7.1	2.3
ethyl 3-(methylthio)-propionate	10.4	3.2
3-(methylthio)-propyl acetate	0.6	0.02
methionol	<0.1	<0.1

which alcohol fermentation by yeast in wines converts S-3-(hexan-1-ol)-L-cysteine (Cys-3MH) into 3MH [149]. Later Peyrot des Gachons et al. discovered a second pathway, whereby the primary precursor to Cys-3MH, termed S-3-(hexan-1-ol)-glutathione (G-3MH) can generate Cys-3MH by the action of  $\gamma$ -glutamyltranspeptidase and carboxypeptidase enzymes [150]. The intermediate in this pathway was confirmed by Jeffery et al. who found S-3-(hexan-1-ol)-L-cysteinylglycine (Cys-Gly-3MH) in Sauvignon blanc grape juice, which was shown to be the precursor to 3MH in this juice [151].

The final proposed mechanism relates to the enzymatic oxidation of lipids to form (E)-2-hexenal, which can react directly with hydrogen sulfide or L-cysteine in the presence of enzymes [152]. This mechanism was confirmed by using deuterated standards of (E)-2-hexenal in wine to form the deuterated-3MH product. This same research article provided a similar mechanism for the formation of 4MMP by using deuterated-mesityl oxide as the precursor which

**Table 19 – The list of pineapple VSCs reported in the literature.**

VSC	Reference
2-(methylthio)-ethyl acetate (tent)	[174]
3-(methylthio)-1-propanol (methionol)	[172,173]
3-(methylthio)-propanal (methional)	[172,174]
3-(methylthio)-propionic acid	[176]
3-(methylthio)-propyl acetate	[169,172,173,174]
diethyl sulfide (tent)	[176]
dimethyl disulfide (DMDS)	[167,176]
dimethyl trisulfide	[170]
ethyl 2-(methylthio)-acetate	[168,172,173,174]
ethyl 3-(methylthio)-(Z)-2-propenoate	[170]
ethyl 3-(methylthio)-propionate	[163,164,168,169,172,173,174,175,176]
ethyl 3-(methylthio)-(E)-2-propenoate	[170,174]
ethyl 4-(methylthio)-butyrate (tent)	[170]
methanethiol (tent)	[176]
methyl 2-(methylthio)-acetate	[167,172,173,174,176,177]
methyl 3-(methylthio)-(Z)-2-propenoate	[170,174,176]
methyl 3-(methylthio)-propionate	[162,163,164,169,172,173,174,175,176,177]
methyl 3-(methylthio)-(E)-2-propenoate	[170,174,176]
methyl 4-(methylthio)-butyrate	[170,174]
methyl mercaptan	[167]
methyl methanethiosulfinate (tent)	[176]
methyl s-methylthiocarbonate	[177]
s-methyl thioacetate	[174]

could explain the biogenesis of this compound in grapefruit, guava, mango, and orange [153]. Later, Harsh et al. continued these mechanistic studies and identified (E)-2-hexenal as another precursor to 3MH and 3MHA in wine, albeit a smaller factor in the formation process [154]. In wine, there appears to be some debate on the most preferred mechanism as a recent study by Subileau et al. found that G-3MH was the major precursor to 3MH, instead of Cys-3MH and (E)-2-hexenal [155]. Wine experiments also identified the mechanism for 3MHA, which involves yeast and the acetyltransferase of 3MH [156].

In 2000, Tominaga & Dubourdieu identified Cys-3MH in passion fruit [157]. The authors exposed the extract containing this precursor to  $\beta$ -lyase (*Eubacterium limosumi*) and identified 3MH, along with 3-mercapto-3-methylbutanol. Both compounds were confirmed in passion fruit by a second analysis where the authors extracted the juice with DCM and trapped the thiols by p-hydroxymercuribenzoate. Additional VSCs were identified, included 3MHA, 3-mercaptohexyl butyrate, and 3-mercapto-3-methylbutylacetate. Most recently, Mattivi et al. described the two metabolic routes for the formation of 3MH in yellow passion fruit by isolating each of the precursors as shown in Fig. 6 [158].

Similar pathways for the formation of 4MMP in grapefruit, guava, mango, and orange are possible either from the S-cysteine or S-glutathione conjugate [159] or through the precursor of mesityl oxide.

Additional biogenesis theories were discussed for the formation of MPO, 3MHA, and 3-(methylthio)-hexanol through 3MH. Tressl & Albrecht proposed three possible routes: the condensation reaction of acetaldehyde and 3MH to form MPO; the esterification of 3MH with a corresponding acid to form 3MHA and other thiohexyl esters; and the methylation of 3MH to form 3-(methylthio)-hexanol [160]. Later, Edwards et al. discovered an enzyme in the mesocarp of passion fruit that could hydrolyze thioesters to their respective thiols [161]. This could also partially explain the formation of 3MH, 3MHA, and the other thiohexyl esters found in passion fruit. The full list of 54 VSCs reported in passion fruit is found in Table 15.

## 17. Pineapple (*Ananas comosus*)

Pineapple is a tropical fruit consumed both fresh and in many cooked or processed applications. The fresh fruit possesses a sweet, tropical, sulfury flavor. The first discoveries in terms of VSCs date back to the 1940s and 1960s when authors identified methyl 3-(methylthio)-propionate and ethyl 3-(methylthio)-propionate [162–164]. These compounds have been reported in thermal reactions of L-methionine and glucose, whereby 3-(methylthio)-propionic acid (oxidation product of methional) is esterified with methanol or ethanol (degradation products of glucose) [165]. The more likely formation based on an enzymatic process during the ripening of the fresh fruit is derived through the transamination of L-methionine (Fig. 7).

New VSCs were also identified in the 1970s and 1980s, including DMDS, methanethiol, methyl 2-(methylthio)-acetate, ethyl 2-(methylthio)-acetate, and 3-(methylthio)-propyl acetate [167–169]. Takeoka et al. measured the odor threshold

**Table 20 – The list of additional tropical fruits with VSCs reported in the literature.**

Fruit	VSC	Reference
Bambangan	s-propyl thiohexanoate (tent)	[178]
Binjai	ethyl 3-(methylthio)-propionate (tent)	[178]
	3-(methylthio)-1-propanol (methionol)	[178]
Cashew apple	dimethyl sulfide	[179]
	dimethyl disulfide (DMDS)	[179,180]
	dimethyl trisulfide	[179]
	2-methylfuran-3-thiol	[180]
	3-(methylthio)-propanal (methional)	[180]
	bis-(2-methyl-3-furyl)-disulfide	[180]
Chempedak	1-(methylthio)-propane (tent)	[181]
	2-hydroxyethyl methyl sulfide (tent)	[181]
	3-(methylthio)-1-propanol (methionol) (tent)	[181]
	2-(methylthio)-ethanal (tent)	[182]
	dimethyl trisulfide (tent)	[182]
	3-(methylthio)-propanal (methional)	[182]
	3-(methylthio)-butanal	[182]
	3-(methylthio)-butanol (tent)	[182]
Cherimoya	2-methylthiophene	[183]
	3-methylthiophene	[183]
	2-ethylthiophene	[183]
	benzothiazole	[183]
Cupuacu	4-methyl-5-vinylthiazole	[184]
	3-(methylthio)-propanal (methional)	[184]
Jackfruit	3-(methylthio)-propanal (methional)	[181]
	2-hydroxyethyl methyl sulfide (tent)	[181]
	3-(methylthio)-hexanol (tent)	[181]
Langsat	2-ethyl-1-hexanethiol (tent)	[42]
Lulo	methyl 3-(methylthio)-propionate	[185,186]
Murici	ethyl 3-(methylthio)-propionate	[187,188,189]
	methyl 3-(methylthio)-propionate (tent)	[187]
	3-(methylthio)-1-propanol (methionol) (tent)	[187,188,189]
Monstera deliciosa	ethyl 3-(methylthio)-propionate	[190]
Mombin	dimethyl sulfone	[191]
	benzothiazole	[191]
	n,n-dimethyl-p-toluenesulfonamide	[191]
Noni	methyl 3-(methylthio)-propionate	[166,192]
	3-(methylthio)-propionic acid (ethylthiomethyl)-benzene	[192]
	methanethiol	[166]
	s-methyl thioacetate	[166]
	dimethyl disulfide (DMDS)	[166]
	ethyl 3-(methylthio)-propionate	[166]
Pomelo	p-1-menthene-8-thiol	[193]
	pentane-1-thiol	[193]
	benzothiazole	[193]
	dimethyl sulfone	[194]

**Table 20 – (continued)**

Fruit	VSC	Reference
Rambutan	2-acetyl-2-thiazoline	[195]
	benzothiazole	[195]
	3-(methylthio)-1-propanol (methionol) (tent)	[195]
	2-acetylthiazole	[195]
	1-propene-1-thiol (tent)	[42]
Sapodilla	benzoyl isothiocyanate (tent)	[42]
Soursop	4-methyl-5-vinylthiazole	[196]
Star fruit	3-mercaptohexanol (tent)	[64]
	2,5-bis-(2-methylpropyl)-thiophene (tent)	[64]

and OAV values for methyl 3-(methylthio)-propionate and ethyl 3-(methylthio)-propionate in the Smooth Cayenne pineapple variety grown in Hawaii (see Table 16).

A couple years later Takeoka et al. produced a second study comparing fresh pineapple to pineapple essence [170]. Methyl 4-(methylthio)-butyrate, identified in the essence extract, was synthesized and its odor threshold in water (133 µg/kg) was measured. Fruit essences require some sort of thermal distillation, therefore methyl 4-(methylthio)-butyrate could form through the thermal reaction of fructose and L-methionine [171]. Using LLE with pentane-DCM, additional research by Elss et al. compared fresh pineapple juice of 19 cultivars from eight different regions to different juice processing conditions (Table 17) [172]. The highest concentration of VSCs was found in fresh pineapple juice. Both juice concentrates from flavor houses and commercial sources showed a significant decrease in the concentration of VSCs.

Several papers studied the concentration of volatile compounds during the ripening process. In the 1990s, Umamo et al. described the difference in volatile compounds from green and ripened pineapples using reduced pressure distillation [173]. A lower concentration of VSCs was measured in the ripened fruit compared to the green, unripe fruit (see Table 18).

Additional studies from pineapples grown in Ghana produced similar results to Umamo et al. where the 12 VSCs identified were generally higher in the green-ripe stage compared to the fully ripe stage [174]. In contrast, Brat et al. compared a hybrid pineapple at 5 different stages of ripening (very green; green; turning ripe; ripe; very ripe) and found only trace VSCs in the green stage and increasing concentrations of VSCs during ripening [175]. Finally, using PFPD, additional studies by Teai et al. in 2001 [176] and Akioka & Umamo in 2008 [177] led to the discovery of new VSCs in the fresh fruit. The full list of 23 VSCs reported in pineapple is found in Table 19.

## 18. Miscellaneous tropical fruits

There are many other tropical and subtropical fruits that contain VSCs reported in the literature, including bambangan (*Mangifera pajang*) [178], binjai (*Mangifera caesia*) [178], cashew apple (*Anacardium occidentale*) [179,180], chempedak

(*Artocarpus integer*) [181,182], cherimoya (*Annona cherimoia*) [183], cupuaçu (*Theobroma grandiflorum*) [184], jackfruit (*Artocarpus heterophyllus*) [181], langsat (*Lansium parasiticum*) [42], lulo (*Solanum quitoense*) [185,186], murici (*Byrsonima verbascifolia*) [187–189], monster deliciosa (*Monstera deliciosa*) [190], mombin (*Spondias mombin*) [191], noni (*Morinda citrifolia*) [166,192], pomelo (*Citrus maxima*) [193,194], rambutan (*Nephelium lappaceum*) [42,195], sapodilla (*Manikara zapota*) [42], soursop (*Annona muricata*) [196], and star fruit (*Averrhoa carambola*) [64]. A table of each fruit's VSCs is shown in Table 20.

## 19. Conclusions

Through intact fruit ripening or secondary enzymatic processes, trace levels of VSCs are formed in certain combinations to help provide the unique aroma for which we can differentiate each fruit. It is not sufficient just to identify VSCs in natural products, as additional analytical and sensory measurements are used to define the contribution these VSCs have to their respective fruit. As an example in the case of orange and grapefruit, p-1-menthene-8-thiol is found in both fresh squeezed juices. Grapefruit juice, however, is considerably more sulfurous in aroma compared to orange juice, which can be attributed to the higher concentration of p-1-menthene-8-thiol, along with the combination of 4MMP. Utilizing selective enrichment methods and instrumentation, researchers aim to identify and quantify these VSCs responsible for the aroma of the natural product. This information can subsequently be used for recombination and omission sensory studies to determine the intrinsic contribution each compound has to the profile of the fruit. As our access to less studied tropical fruits increase, research can utilize the methods described in this review to identify trace level, high impact compounds like VSCs and the contribution each has to the aroma and flavor profile. This information can also be used to optimize breeding and fruit cultivation practices to provide unique sensory characteristics.

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