Aroma Chemicals for the Sweet Field

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The sweet field in the flavors business has been defined[1] as including:

soft drinks
alcoholic beverages
chocolate, flour and sugar confectionery
ice cream
chewing gum

None of the above are the essentials of life, but this makes them no less desirable. Indeed, we may say that they are the stuff of La Dolce Vita, the sweet life. Aroma chemicals for sweet flavors have been available since the discovery of vanillin and the simple esters, but the ever-increasing sophistication of the consumer puts constant demands on the flavorist and the producers of aroma chemicals. In recent years particular areas of interest have included:

- Exotic and "fantasy" flavors; for example, tropical fruit flavors for soft drinks.
- Low-fat and low-calorie products for consumers wanting a full flavor without fat and sugar.
- Low-in-fruit-acids drinks; such as soft drinks, usually for children, which lack the high acidity of traditional juice-based drinks (such as citrus and blackcurrant drinks), and are aimed at the dental health market.
- Flavored waters; usually mineral waters with a fruit flavor lacking sugar or sweeteners.
- Alcoholic drinks with "soft" flavors; the so-called "Alcopops". Simple alcoholic lemonade-type drinks were popular in Britain in the mid-90's, but this led to questions on the ethics of marketing a drink which could target a very young market. This has led to more sophisticated "adult" flavors in these drinks.

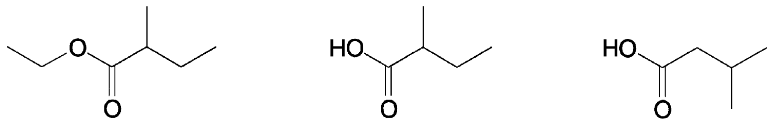

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Figure 1. Fruity esters

The range of flavors here is vast, so this short article will try to comment on some newer developments in the three important areas; traditional fruit-type, chocolate and tropical flavors.

Apple

Apple has been the archetypal fruit ever since the day that, "Eve did eat of the apple," to the legend of Johnny Appleseed. In turn, a key component of apple flavors is the archetypal "fruity" ester, ethyl 2-methyl butyrate (1). Available in both natural and synthetic forms, it is a key compound in apple and fruit formulations. A large number of C_5 acids, aldehydes, alcohols and esters are found in apple juice, with the 2-methyl but- forms predominating.

In fresh apple juice[2], 2-methylbutyric acid (2) predominate over 3-methyl butyric acid (isovaleric acid) (3) by a ratio of up to 99:1. However, in ciders and apple liqueurs the level of isovaleric rises to constitute up to 20% relative to 2-methylbutyric acid. This is believed to be due to microbial action. This change gives the flavorist a possible method of differentiating fresh juice and apple cider flavors.

The second aspect of apple is its freshness. This derives from the so-called "C_6 wound compounds", *cis*-3-hexenol

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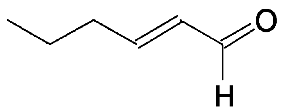
(leaf alcohol) (4), *trans*-2-hexenal (leaf aldehyde) (5), *trans*-2-hexenol (6) and derivatives such as *cis*-3-hexenyl butyrate (7).

These compounds, several of which are available as natural materials, are formed during tissue damage when linoleic acid acts as a trap for peroxide radicals and in doing so is cleaved to the unstable *cis*-3-hexenal, which is rearranged and/or reduced to give the stable aldehydes and alcohols.



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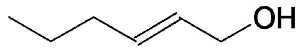

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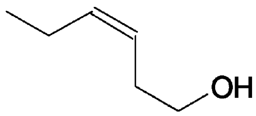

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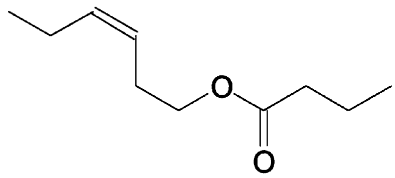

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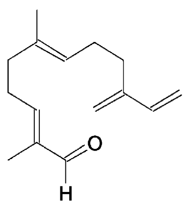
Figure 2. C_6 wound compounds

Citrus

The ready availability of orange oil as a by-product of the vast juice business makes this the most common source of orange flavors. Orange oil consists largely of the virtually odorless limonene. The zestiness of orange oil is due to trace components, particularly aldehydes such as octanal through to undecanal, and the sinesals (β-sinesal (8) in orange oil, α-sinesal in mandarin). Unsaturated aldehydes, especially *trans*-2-decenal (9) have a combined fatty-citrus character reminiscent of orange zest. In lemon, terpenes such as citronellol (10) and citral are important.



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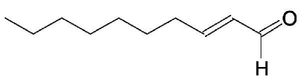

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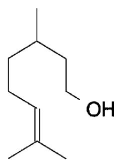

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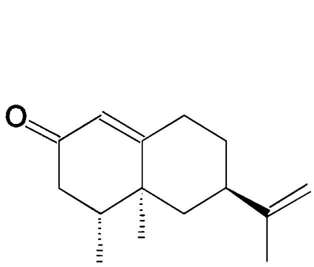
Figure 3. Citrus compounds

In grapefruit, two compounds have been credited with character impact. Initially nootkatone (11) was believed to be the most important, but other work[3] has indicated that whilst it may be important in grapefuit oil, the smaller and less hydrophobic 1-p-methene-8-thiol (grapefruit mercaptan) (12) is probably the key character-impact compound in the juice[4]. This intensively odorous material has been described as extremely diffusive[5,6] and has an extraordinarily low odor threshold of 0.01 ng/L.



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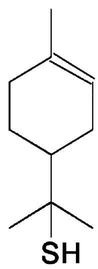

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Figure 4. Molecules with grapefruit character

Blackcurrant

Blackcurrant flavors are often associated with health drinks. High in Vitamin C, it is often associated with the neutraceutical area of flavors. The characteristic cattiness of blackcurrant is derived from 4-methoxy-2-methyl-2-butanethiol (blackcurrant mercaptan) (13), which has been identified in olive oil and is found at 0.2ppb in blackcurrant liqueur. Other compounds that can be used are 8-mercapto-p-menthan-3-one (thiomenthone) (14), found in Buchu leaf oil, and 4-mercapto-4-methyl-2-pentanone (cat ketone) (15). The latter, with an extremely low odor threshold of 3 mg/L, has been found in Sauvignon grapes[7] and contributes to the musky cattiness of that wine.

Soft Fruits: Strawberry and Raspberry

These have long been popular flavors for soft drinks, candy and chewing gum. The first compounds to be used for this were ethyl 3-methyl-3-phenylglycidate (strawberry aldehyde, aldehyde C-16 so-called) (16) and ethyl 3-phenylglycidate (raspberry aldehyde, aldehyde C-20 so-called) (17). These materials, which have not been found in nature, give characteristic, pleasant flavors that have been described as red rather than strawberry or raspberry. In an article on the glycidates[8], a comment was made that, "Until the 60s, [the glycidates] were used in various parts of the world to create the flavor of these wonderful hard candies whose flavor we now call red." At the same time, in Britain, all strawberry and raspberry-flavored drinks were described by children as "red pop", irrespective of the flavor claimed on the label.

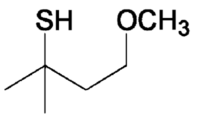
Today, people expect flavors to be more realistic and nature-identical molecules are the key to this. Major components are often hydroxydimethyl furanone (furaneol, strawberry furanone) (18) together with methyl cinnamate (19) (both of these are available in natural forms) and hydroxyphenylbutanone (raspberry ketone) (20).

A recent paper on strawberry juice[9] analyzed the top flavor-active components and put together a formulation based on the top odor-active materials (Table 1). By successively excluding components from this, the importance of hydroxydimethyl furanone and *cis*-3-hexenal was shown. In the absence of the former, the greenness of the aldehyde dominated the formulation. In the absence of the latter, the cotton-candy, caramel flavor of the furanone was predominant. Methoxydimethyl furanone, whose absence was scarcely noted in the formulation, is the methyl ether of hydroxydimethyl furanone and has a similar odor, and so its contribution would be overwhelmed by the latter.

We may also consider strawberries swimming in the cream[10], a common adjunct to soft fruits since at least the 16th century. The impact of adding cream to (heated) raspberries (unfortunately we have no report on its effect on strawberries) was studied by GC-olfactometry[11]. This found that the impact of the four most potent odorants, β-damascenone (21), vanillin (22), sotolone (23), 1-nonen-3-one (24) and the character impact compound hydroxyphenylbutanone (19) all fell when cream was added.

Chocolate

"Mmmmmm…chocolate…."[12] Chocolate is probably the world's favorite flavor. It is very complex, with extensive processing in the creation of the flavor. The key step is the



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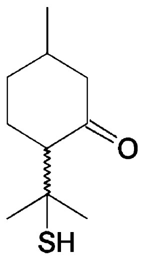

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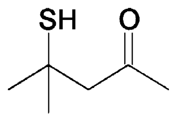

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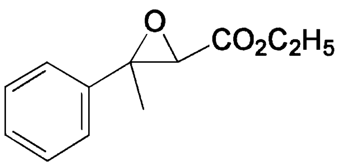
Figure 5. Catty, blackcurrant compounds



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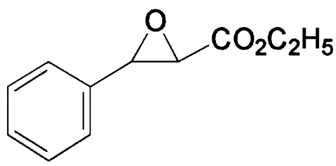

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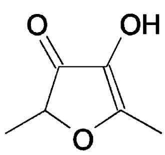
Figure 6. Artificial glycidates for strawberry and raspberry



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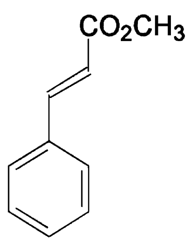

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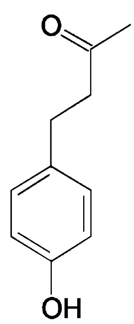

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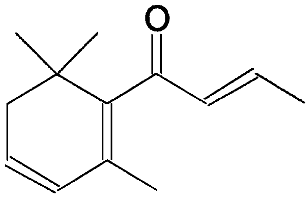
Figure 7. Nature-identical molecules for strawberry and raspberry



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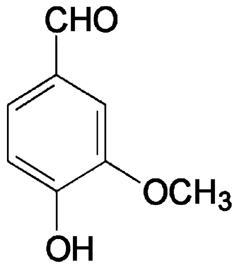

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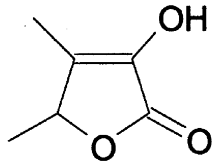

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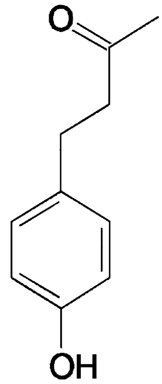

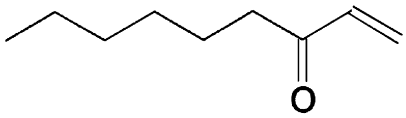

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Figure 8. Raspberry flavor components affected by cream

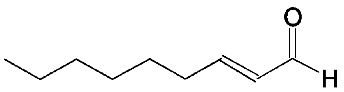
Table 1. A formulation based on the top 12 odor-active volatiles in strawberry juice

	When omitted from the formulation, how many people (from six) noticed?	
	By Odor	**By Taste**
Hydroxydimethylfruanone	6	6
Cis-3-hexenal	5	5
Methyl Butyrate	4	3
Ethyl Butyrate	4	3
Ethyl 2-Methyl Butyrate	4	4
Acetic Acid	3	3
Diacetyl	3	2
Butyric Acid	2	3
2-Methylbutyric Acid	2	1
Ethyl Isobutyrate	2	1
Methoxydimethylfuranone	1	0

roasting of the cocoa bean to create the cocoa mass; here the Maillard reaction takes place leading to the formation of Strecker aldehydes, pyrazines, furans and sulphur compounds. Aroma-extract dilution analysis of a milk chocolate[13] has shown the top-most important active volatiles to be those in Table 2. The aldehydes and pyrazines are typical of a Maillard reaction, and the resemblance to a savory flavor is striking[14]. *Trans*-2-nonenal (25) and *trans*-2-*trans*-4-decadienal (26) have very fatty odors, and methyl (2-methyl-3-furyl) disulphide (27) is better known in the context of meat and savory flavors. The pyrazines (28 and 29) have a roasted character. 5-Methylhept-2-en-3-one (filbertone) (30) probably derives from added nuts.

Table 2. Aroma-extract analysis on milk chocolate

Compound	Odor, Character	Compound	Odor, Character
Isovaleraldehyde	Malty, Sharp	2,3-Diethyl-5-Methylpyrazine	Potato-Chip
2-Ethyl-3,5-Dimethylpyrazine	Potato-Chip	*Trans*-2-Nonenal	Green, Tallow
2-Methylbutyric Acid	Sweaty	*Trans*-2-*Trans*-4-Decadienal	Fatty, Waxy
Isovaleric Acid	Sweaty	*Trans*-2-*Trans*-4-Nonadienal	Fatty
5-Methylhept-2-En-3-One	Hazelnut	γ-Decalactone	Sweet, Peach
1-Octen-3-One	Mushroom	Methyl (2-Methyl-3-Furyl) Disulphide	Sulphurous, Meaty
2-Ethyl-3,6-Dimethylpyrazine	Nutty, Earthy		



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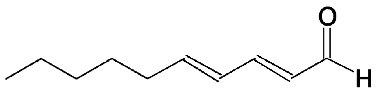

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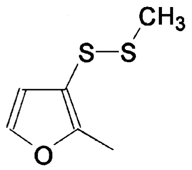

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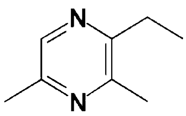

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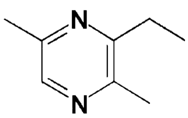

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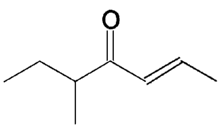

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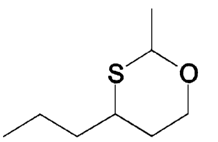
Figure 9. Some important chocolate aroma chemicals



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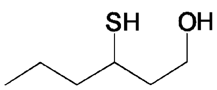

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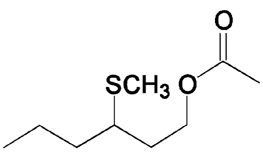

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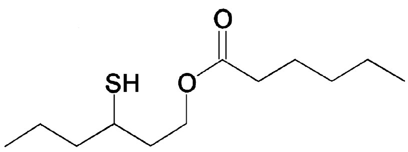

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Figure 10. Sulphur compounds in passionfruit

Tropical Flavors

Flavors derived from tropical fruits such as passion fruit, lychee and kiwi-fruit have been very successful in recent years. Indeed, the popularity of the flavors exceeds the popularity of the fruits themselves, which can be expensive, and may be rather unattractive in the flesh; especially passion fruit. If apple is the archetypal northern fruit, then passion fruit is the archetypal tropical fruit.

Analysis of passion fruit[15] reveals a whole suite of sulphur-containing molecules, some of which are shown in Figure 10. 2-Methyl-4-propyl-1,3-oxathiane (Tropathiane) (31) is the best known of these. The closely related 3-mercapto-1-hexanol (passion fruit mercaptan) (32) has an intense sulphurous odor with a powerful passion-fruit character on dilution. Like grapefruit mercaptan mentioned earlier, it is an intensely diffusive molecule. 3-Methylthiohexyl acetate (33) is less powerful and has a more fragrant lychee note.

A large number of tropical sulphur compounds were included in the GRAS 18 list, published by FEMA in 1998. These included a number of molecules such as 3-mercaptohexyl hexanoate (34), which have a free mercaptan group γ- to an ester. Whilst these molecules are stable in the pure form, their long-term stability in a formulation is questionable. When 3-acetylthiohexanal (35) was reduced with sodium borohydride[16], instead of the single product we expected, we found four, due to intra- and inter-molecular acyl transfer (Figure 11).

This phenomenon, which we dubbed the OAc-SAc shuffle, is particularly facile for the 1,3-subsituation pattern where the intra-molecular reaction occurs via a stable cyclic intermediate with a low-energy transition state (Figure 12). Whilst the reaction shown is for alkaline conditions, this intra-molecular esterification will also be subject to acid catalysis, and hence the long-term future of 3-mercaptoalkyl esters in any formulation is uncertain.

This 1,3-oxygen, sulphur functionality is actually found in a number of intensely odorous molecules (Figure 13). The carbon framework varies in length and branching and includes ring structures, but this "odorophore" is always present. It is found in its simplest form in the passion fruit mercaptan (32), as a thioacetal in tropathiane (31), as a mercapto ether in the black currant mercaptan (13), as a mercapto ketone in thiomenthone (14) and as an alkylthio-ester in (35), the so-called pineapple mercaptan. A putative biosynthetic route is Michael addition of a sulphur nucleophile to an α,β-unsaturated carbonyl compound, followed by further transformations, including the OAc-SAc shuffle (Figure 14).

Durian: A Fruit Too Far

Whilst flavorists reach ever further into new and exotic areas to meet the expanding tastes of the consumer, durian remains a fruit too far. It is popular in South East Asia amongst people who have grown up with it, however, its gassy, sweetcorn-in-a-sewer odor is highly unattractive to most people.

However, it is rich in sulphur compounds[17] with potential FEMA GRAS status. A number of ethyl sulphides such as the disulphide (36) contribute the repellent, gassy note. Better-known sulphur compounds such as 2-isopropyl-4-methyl thiazole (37) are also present. Methyl thiohexanoate (39), one of the compounds on FEMA's GRAS 18 list, has been found in durian. It has an intense sweet, ripe, odor with tropical and soft-fruit notes. While it may be used to re-create a durian flavor, strawberry, pineapple and passion fruit, there are more likely destinations.

Conclusion

This brief survey has tried to illustrate the range of aroma chemicals for the sweet field. This will continue to expand as consumers demand more exotic flavors, more realistic versions of established flavors and as more aroma chemicals become available to the flavorist's palate.

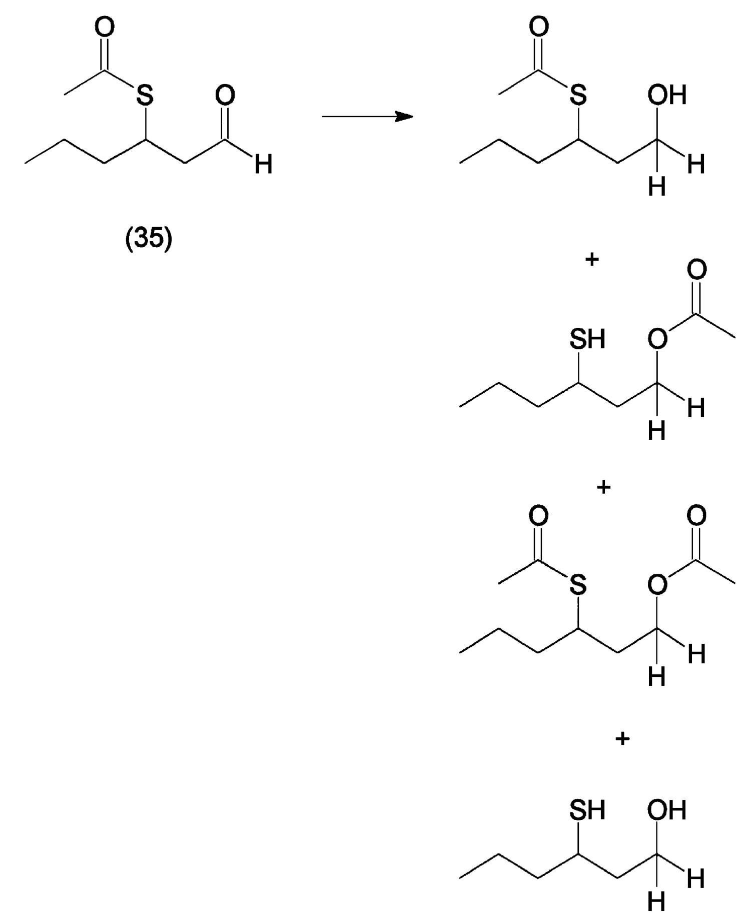

Figure 11. Compounds formed during the reduction of 3-methylthiohexanal

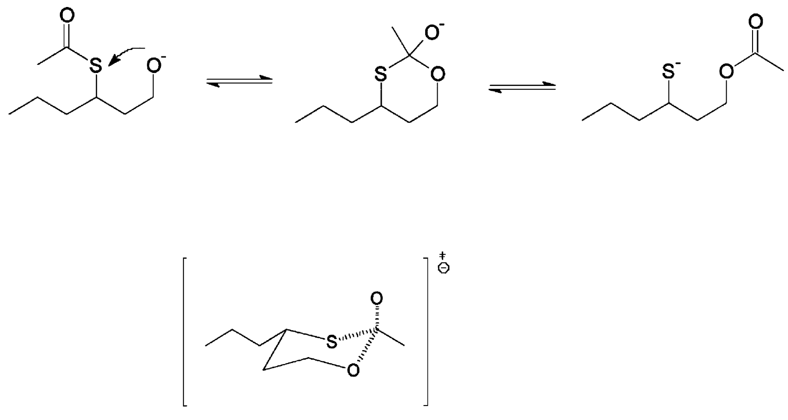

Figure 12. The OAc-SAc shuffle

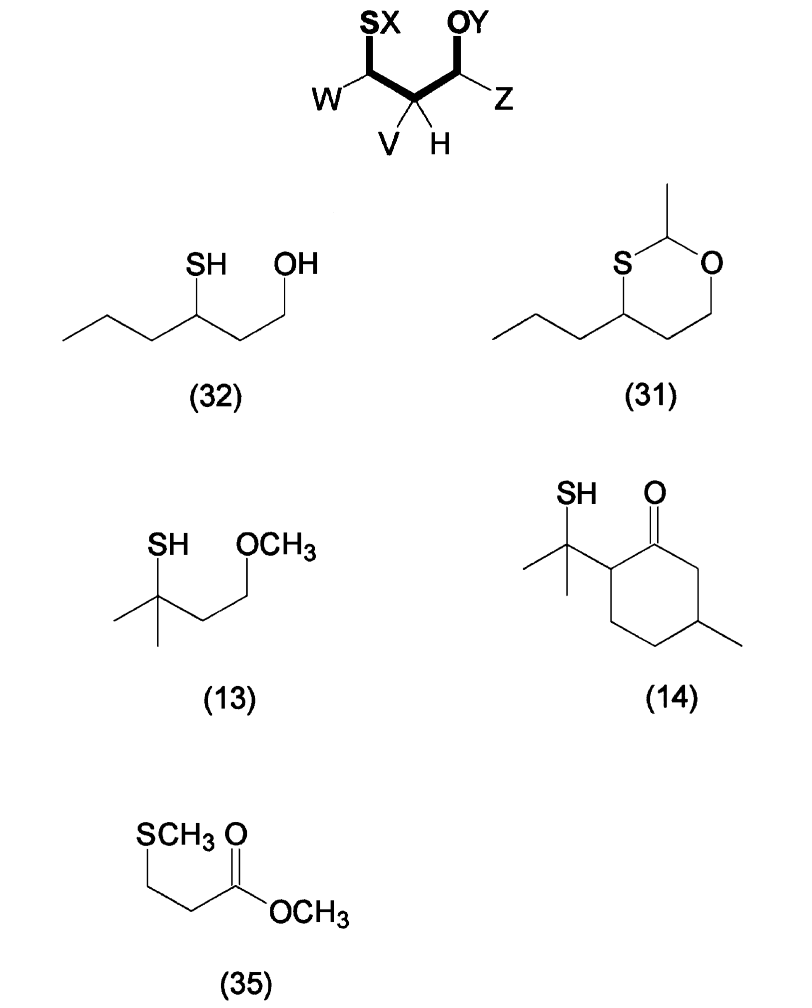

Figure 13. The 1,3-oxygen, sulphur "odorophore"

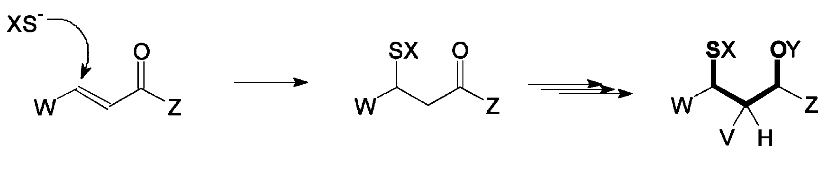

Figure 14. Synthesis of the 1,3-oxygen, sulphur "odorophore"

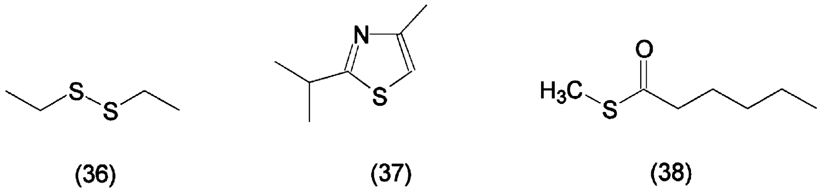

Figure 15. Durian compounds

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