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From the Experts

High Impact Aroma Chemicals Part III

Fire and brimstone: sulfur aroma chemicals

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Oxford Chemicals Ltd.

Mention the word “sulfur” to the general public and the response is unlikely to be favorable. In terms of bad press, sulfur is up there with plutonium, only it has had many more years to get instilled into our psyche as bad news. Nearly four centuries separate the English playwright William Shakespeare from the American poet Anne Sexton, but both can use this element to generate the sense of menace and horror (see sidebar). Yet in terms of flavor and fragrance chemistry, many of our most popular foods rely on sulfur compounds for their character.¹⁻³ If we consider the elegant meal at our hypothetical restaurant, “La Belle Isis” (named for the river which flows through the city of Oxford), we can see that from truffles to the choice of wine there are key aroma chemicals containing sulfur (F-1).

Lest this be interpreted as a bit Marie Antoinette (“let them eat truffles”), we can illustrate the same theme via a more down-to-earth virtual establishment, “The Greasy Ox” (F-2); this might still be considered a Homeric meal, though here the Homer would be Simpson.

And thirdly, we can move away from the Europe/North America axis by considering Indian foods, or perhaps to be more accurate, some of the Indian foods popular in Britain; here, the name derives from Petigara Chemicals, Oxford’s agent in India (F-3).

These three examples go some way toward illustrating the range of applications for sulfur aroma chemicals. If we now turn to chemical types, we can define our sulfur aroma chemicals a little more precisely. First of all, we can eliminate some sulfur chemicals, which, though important, would not be considered aroma chemicals per se:

- i. The sulfur-containing amino acids, methionine and cysteine. These are involatile, and would not generally be considered aroma chemicals; they will contribute some flavor in their own right, but are probably most important as precursors to aroma chemicals via the Maillard reaction.
- ii. Reactive precursors such as allin, which generate the important aroma chemicals.
- iii. Isothiocyanates, especially allyl iso-

“Ye devils...

Roast me in sulphur!

Wash me in steep-down gulfs of liquid fire!”

—William Shakespeare, 1564-1616

“I hear the death of me,

The murderous weeds,

The stallion breathing sulfur...”

—Anne Sexton, 1928-1974

“Let them eat truffles”

F-1

DEJEUNER A LA BELLE ISIS

METHYL PROPYL DISULFIDE BIS(METHYLTHIO)METHANE

ONION SOUP WITH TRUFFLES

2-MTHEYL-3-FURANTHIOL ALLYL DISULPHIDE

ROAST BEEF IN A GARLIC SAUCE

2-ISOPROPYL-4-METHYLTHIAZOLE= TROPATHIANE

PEACH & PASSION FRUIT SORBET

4-METHYL-4-MERCAPTO-2-PENTANONE

CABERNET SAUVIGNON

DINNER AT THE GREASY OX

2-METHYL-3-FURANTHIOL FURFURYL MERCAPTAN

BURGER ON A SESAME SEED BUN

2-ISOBUTYLTHIAZOLE

TOMATO KETCHUP

METHIONAL

LARGE FRIES

FURFURYL MERCAPTAN

REGULAR COFFEE

DINNER AT THE PETIGARA CURRY HOUSE

METHYLPROPYLTRISULPHIDE FURFURYL MERCAPTAN

ONION BAHJI

METHIONAL

SAG ALOO

ALLYL DISULPHIDE

GARLIC NAN

PRENYL MERCAPTAN

GLASS OF BEER

thiocyanate, which is an important component for mustard, but is more of a trigeminal stimulant leading to a sensation rather than an aroma.

This still leaves a good range of functionality, i.e.:

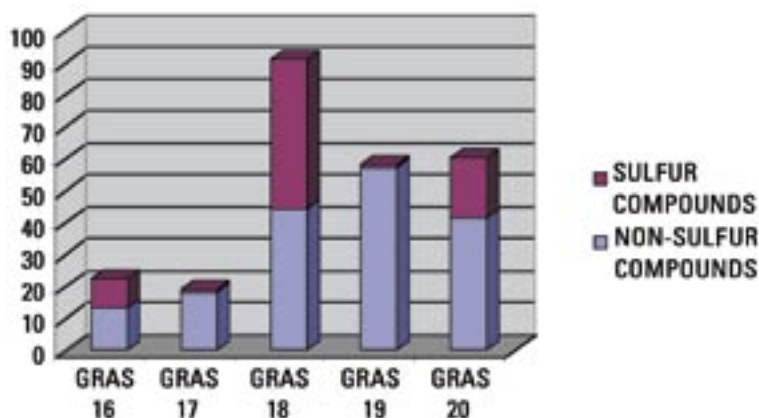
- Mercaptans (thiols)
- Sulfides
- Di-, tri- and higher sulfides
- Thioesters
- Thiophenes
- Thiazoles
- Dithiazines

This group still encompasses a huge number of chemicals, so to narrow down further the most actively developing areas we can look at recent FEMA GRAS listings. Compounds on these lists have at least been considered sufficiently interesting for companies to expend the time and money needed to fulfill FEMA's requirements. If we consider the last 10 years, from 1993's GRAS 16 to 2001's GRAS 20, we can see that sulfur compounds, especially in the large GRAS 18 list, are disproportionately represented (F-4).

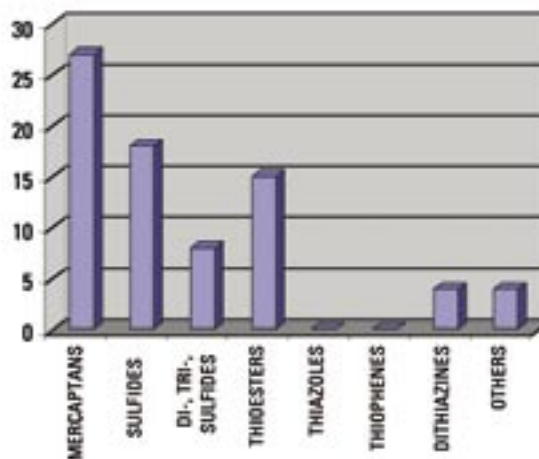
We can break this down further by considering the types of sulfur molecules (F-5).

In F-5 we can see that five groups have dominated recent lists: mercaptans, sulfides, di- and tri-sulfides,

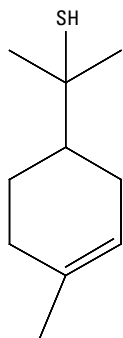
New FEMA GRAS sulfur compounds 1993-2001



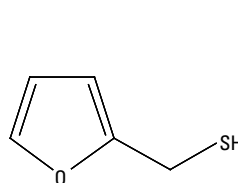
Sulfur functionalities in new FEMA GRAS compounds 1993-2001



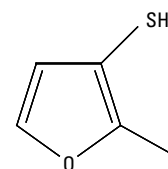
P-MENTHEN-8-THIOL (GRAPEFRUIT MERCAPTAN)



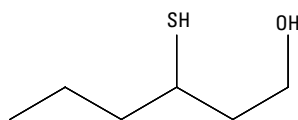
FURFURYL MERCAPTAN



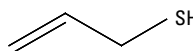
2-METHYLFURAN-3-THIOL (MFT)



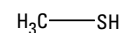
3-MERCAPTO-1-HEXANOL



ALLYL MERCAPTAN

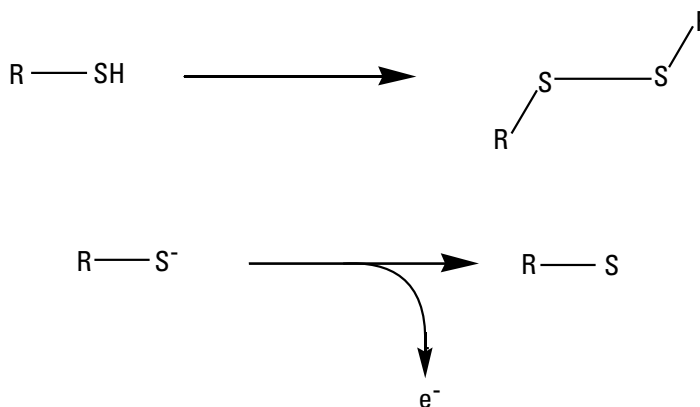


METHYL MERCAPTAN



Oxidation of mercaptans

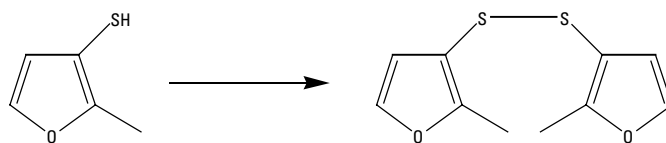
F-7



thioesters and dithiazines. This does not imply any lack of importance for other groups such as thiazoles, but that these are “mature” aroma chemicals that have been in use for some years and are well known and understood. Hence the remainder of this discussion will concern the “top three,” and in particular, some of the stability aspects associated with using these materials, in both flavor and fragrance formulations. This is of special interest in that the high odor of

these materials means that they are used in formulations at very low levels, and hence monitoring any chemical changes that may take place post-formulation is very difficult. In addition, the chemical complexity and difficulty of handling of some of these materials means that they are expensive per kilo, and people want to be sure they are getting their money’s worth!

2-METHYL-3-FURANTHIOL

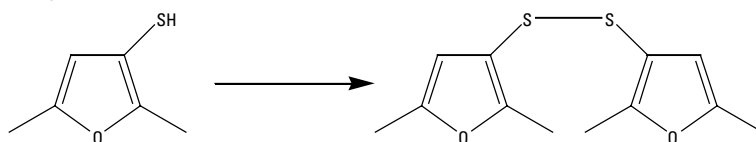


IN PG, OXIDIZES ~50% AND THE ODOR FADES

IN TRIACETIN, LESS OXIDATION BUT STILL APPRECIABLE ~30%

BEST NEAT

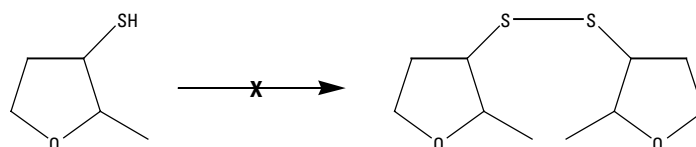
2,5-DIMETHYL-3-FURANTHIOL



RAPIDLY OXIDIZED; GOES DARK RED, COMES OUT OF SOLUTION AS THE DISULFIDE. STAYS IN SOLUTION IN TRIACETIN, 60% CONVERSION TO DISULFIDE

NEAT; GOES CLOUDY DUE TO WATER PRODUCTION UNLESS STABILIZER ADDED (α -TOCOPHEROL)

TETRAHYDRO-2-METHYL-3-FURANTHIOL



NO OXIDATION

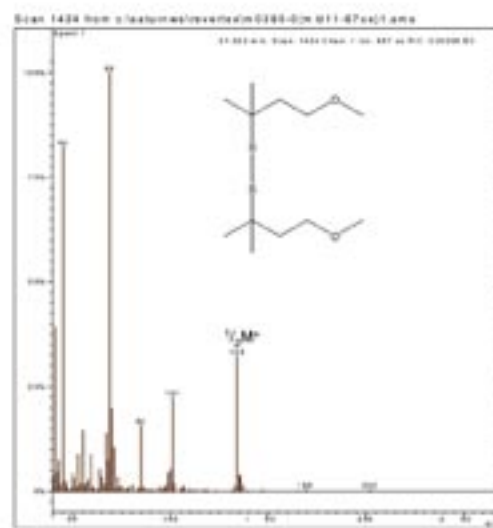
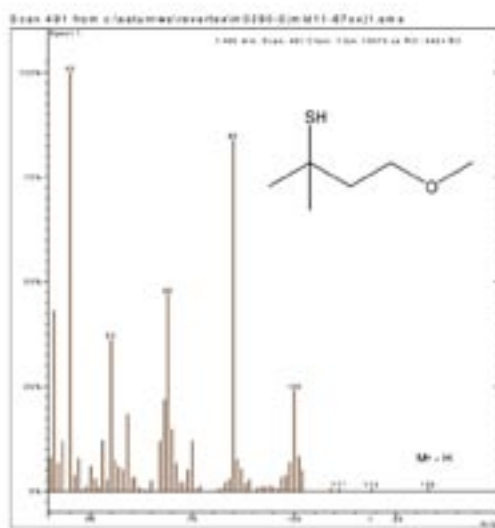
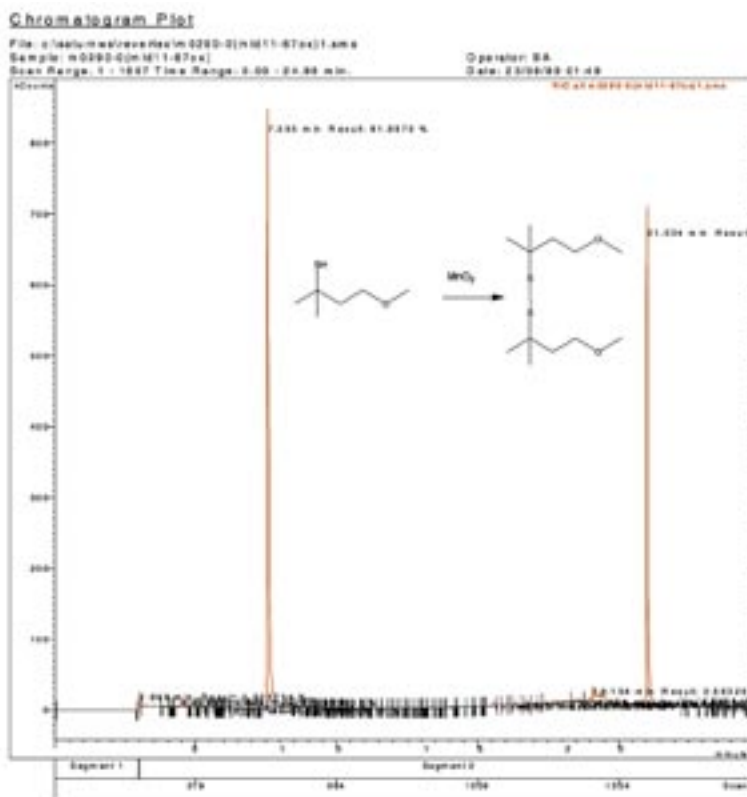
REACTIVITY OF A 2° ALIPHATIC MERCAPTAN

Mercaptans

The range of mercaptans used in the flavor and fragrance industry is wide, in terms of applications and chemical structure, as shown in F-6.

These are generally the most odorous of all aroma chemicals, with thresholds below 1 ppb and falling to as low as 10^{-4} ppb. The most common problem associated with

their use is oxidation, usually to the corresponding disulfide, which typically will have a lower impact due to both its higher molecular weight (and hence lower volatility) and an inherently lower odor threshold. This reaction, which in some cases can take place simply on contact with air, is a free radical reaction occurring via loss of an electron; this will take place more readily from the mercaptide anion, and hence the tendency towards oxidation increases with pH (F-7).



Having said all this, the tendency towards oxidation is highly variable. Since electron loss is key to oxidation, those mercaptans that are electron-rich will show a greater tendency to oxidation. We can see this with the furanthiols, where the thiol function is in conjugation with the π -excessive furan ring (F-8).

Both MFT and DMFT oxidize rapidly in solution in the absence of any stabilizer, with DMFT, whose extra methyl group contributes further to the electron

density of the ring, oxidized the faster of the two. We can see that this is indeed due to the electron-rich nature of the system and not to any other factors by the observation that this reactivity is not seen in tetrahydro MFT; here the π -system is absent, and the reactivity is that of a secondary aliphatic mercaptan (F-9).

4-METHOXY-2-METHYL-2-BUTANETHIOL

Application	pH	Dilution	WW	BC	Odor at 4°C	Odor at 25°C	Odor at 40°C	Odor at 25°C Daylight	Color at 40°C	Color at 40°C Daylight	Comments	Final Judgement
ACID CLEANER	1	0.01% in DPG	1	1	G	G	G	G	G	G	Good Blackcurrant	G
CREAM RINSE	3.5	0.01% in DPG	0.3	2	G	G	G	G	G	G	Very Good Blackcurrant	E
TOILET CLEANER	4	0.01% in DPG	0.2	2	M	R	R	R	G	G	Off	R
DEO STICK	4.3	0.01% in DPG	1	0.5	G	G	M	R	G	G	Off	R
FABRIC SOFTENER	4.5	0.01% in DPG	0.3	2	G	G	M	M	G	G	Weak	M
DEO PUMP SPRAY	6.6	0.01% in DPG	1	0.5	G	G	G	G	G	G	Good Fruit	G
EAU DE TOILETTE 65%	7.1	0.01% in DPG	5	2	G	G	G	G	G	G	Fruit Berry	E
HAND CREAM	7.5	0.01% in DPG	0.5	0.5	G	G	G	G	G	G	Fruit Berry	G

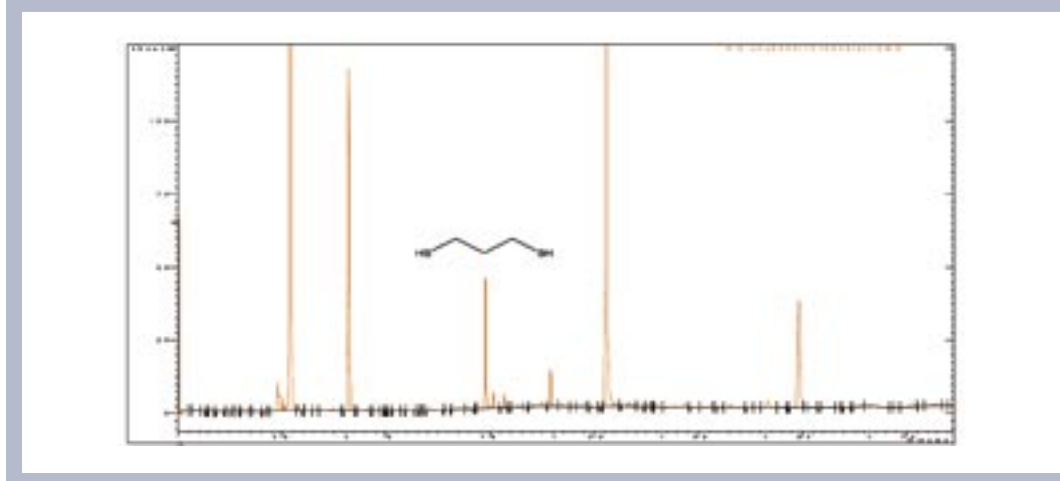
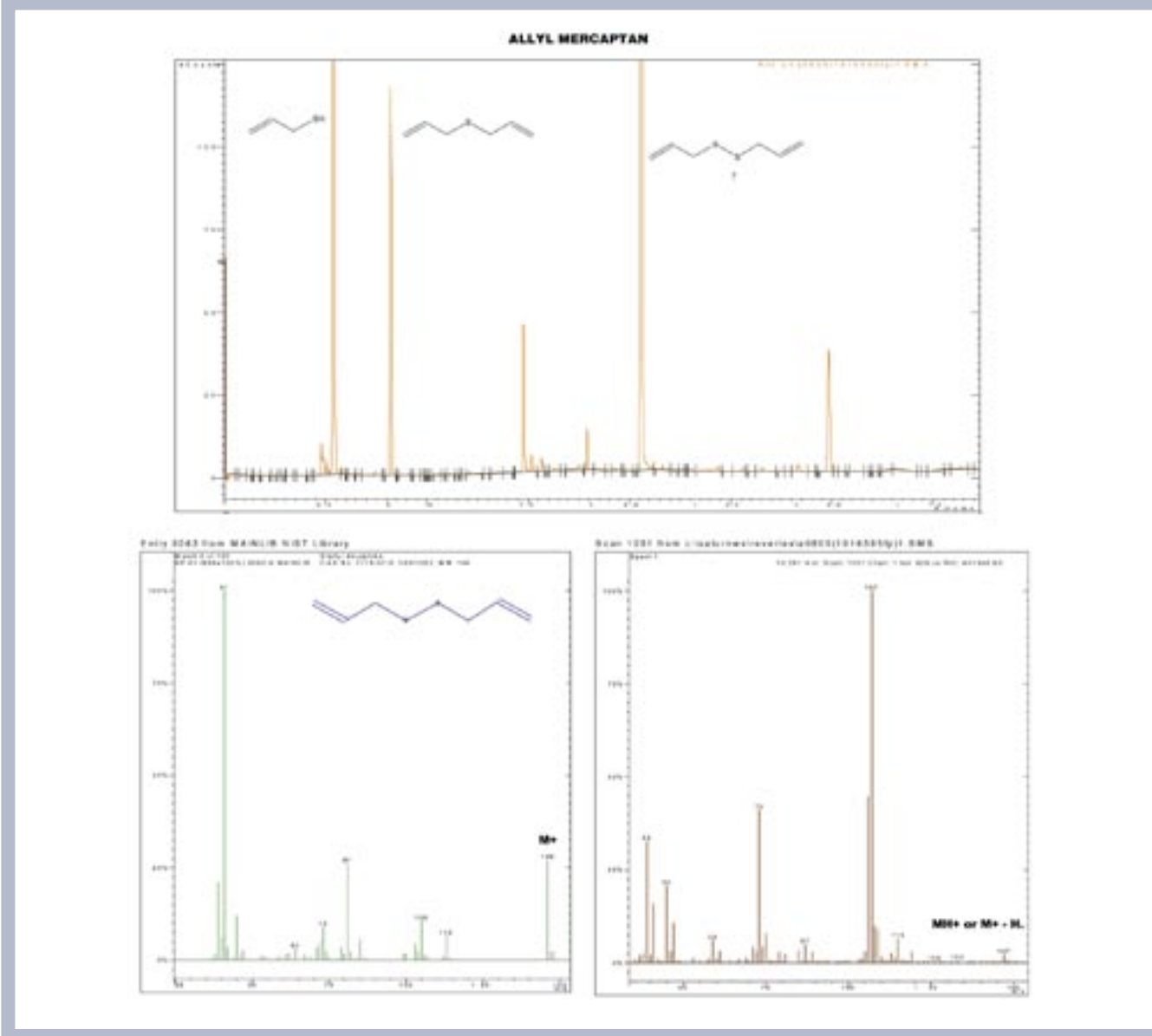
4-METHOXY-2-METHYL-2-BUTANETHIOL

Application	pH	Dilution	WW	BC	Odor at 4°C	Odor at 25°C	Odor at 40°C	Odor at 25°C Daylight	Color at 40°C	Color at 40°C Daylight	Comments	Final Judgement
LIQUID DETERGENT	7.8	0.01% in DPG	0.4	0.5	G	G	G	G	G	G	Fruit Berry	G
SHAMPOO	6.3	0.01% in DPG	0.5	1	G	G	G	G	G	G	Fruit	G
TALC	9.7	0.01% in DPG	1	0	M	M	R	R	G	G	Off	R
BAR SOAP	10.2	0.01% in DPG	1.5	1	G	G	G	M	G	G	Fruit Weak	M
ALL PURPOSE CLEANER	10.4	0.01% in DPG	0.2	0	M	M	M	M	G	G	OK to Use Weak	M
DETERGENT POWDER	10.9	0.01% in DPG	0.2	1	G	G	R	G	G	G	Off	R
COMPACT DET. POWDER	11	0.01% in DPG	0.4	2	G	M	M	M	G	M	OK to Use	M
LIQUID BLEACH	11	0.01% in DPG	0.2	1	M	R	R	R	G	G	Off	R

In the absence of any other factors, the tendency to oxidation is determined by steric factors, i.e. primary > secondary > tertiary. Tertiary mercaptans can be remarkably resistant to oxidation. A sample of the blackcurrant/cassis mercaptan, 4-methoxy-2-methyl-2-butanethiol that had been stored for several years appeared to show no oxidation by GC. To ensure that

we were simply not detecting the disulfide, we treated a sample with manganese dioxide. This performed the oxidation, but again, with less vigor than expected in that only ca. 30 percent of the disulfide was formed. GC and GC/MS showed that, indeed, no oxidation had occurred in the sample despite long storage (F-10).

This chemical stability means that it can be very useful in demanding media, especially some of those used in the fragrance industry. Stability studies showed



it to give excellent results, especially under neutral and acidic conditions. The failure of performance in alkaline conditions merely reflects the acidity of the thiol function, i.e. at high pH the molecule is deprotonated to give the involatile mercaptide ion (F-11: E = Excellent, G = Good, M = Moderately successful, U = Unsuccessful).

All the observations described above fit the expected patterns, but of course, in general, we should be wary of generalizations! This is illustrated by the case of allyl mercaptan. This is one of the most recalcitrant molecules to work with, in that the purity falls rapidly on storage. This was always assumed to be due to oxidation to the disulfide. However, the reaction seemed to be occurring much faster than we should expect for an aliphatic mercaptan (the double bond in allyl mercaptan is not in conjugation with the thiol group, and hence this is not an especially electron-rich molecule). A second concern was that the reaction seemed to be producing a number of compounds; simple oxidation should give the disulfide and nothing else (the allyl sulfide shown on the trace is a by-product of synthesis). On GC/MS the peak, which had always been assumed to be allyl disulfide, did not give a good match (F-12); confirmation that it was not the disulfide was shown by “spiking” a sample with authentic disulfide.

A clue as to the nature of the reaction came from the identification of a smaller peak, which was found to be 1,3-propanedithiol (F-13), the presence of which is best explained by free radical addition of hydrogen sulfide to allyl mercaptan.

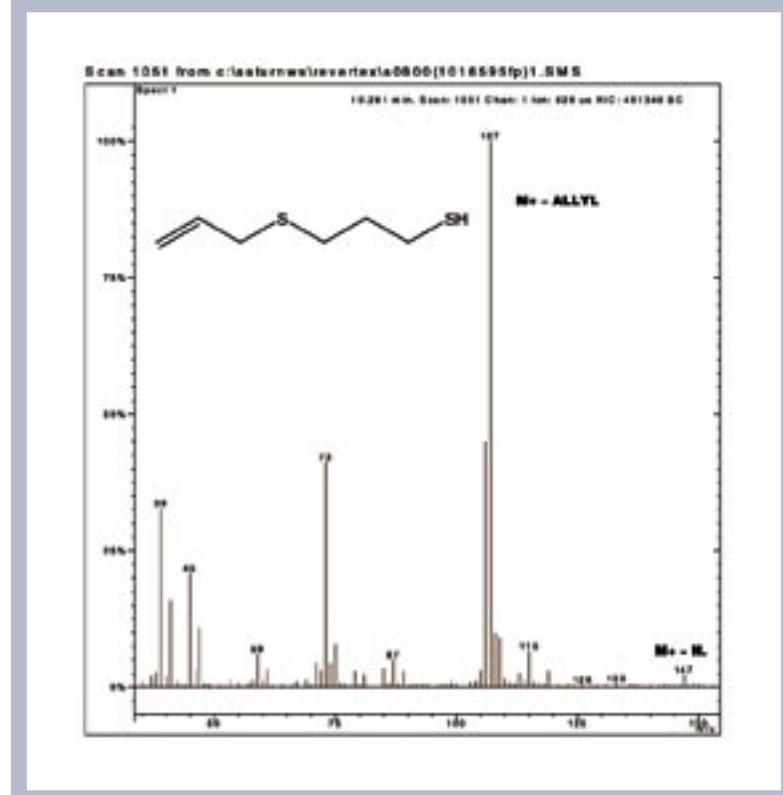
With this in mind, we can explain the main peak [3-(allylmercapto) propane-1-thiol (F-14)] as the free radical addition product of one allyl mercaptan molecule to the double bond of another.

This also explains the “extra peaks” that develop. We also see further addition of products, with the back peak identified as a triple adduct (F-15).

No doubt we would see further products if we ran the GC for longer, as what is occurring is a very slow polymerization (F-16). This is not strictly an oxidation, but since this is almost certainly a free radical reaction, it will be still be initiated by an oxidation of the thiol group.

Sulfides

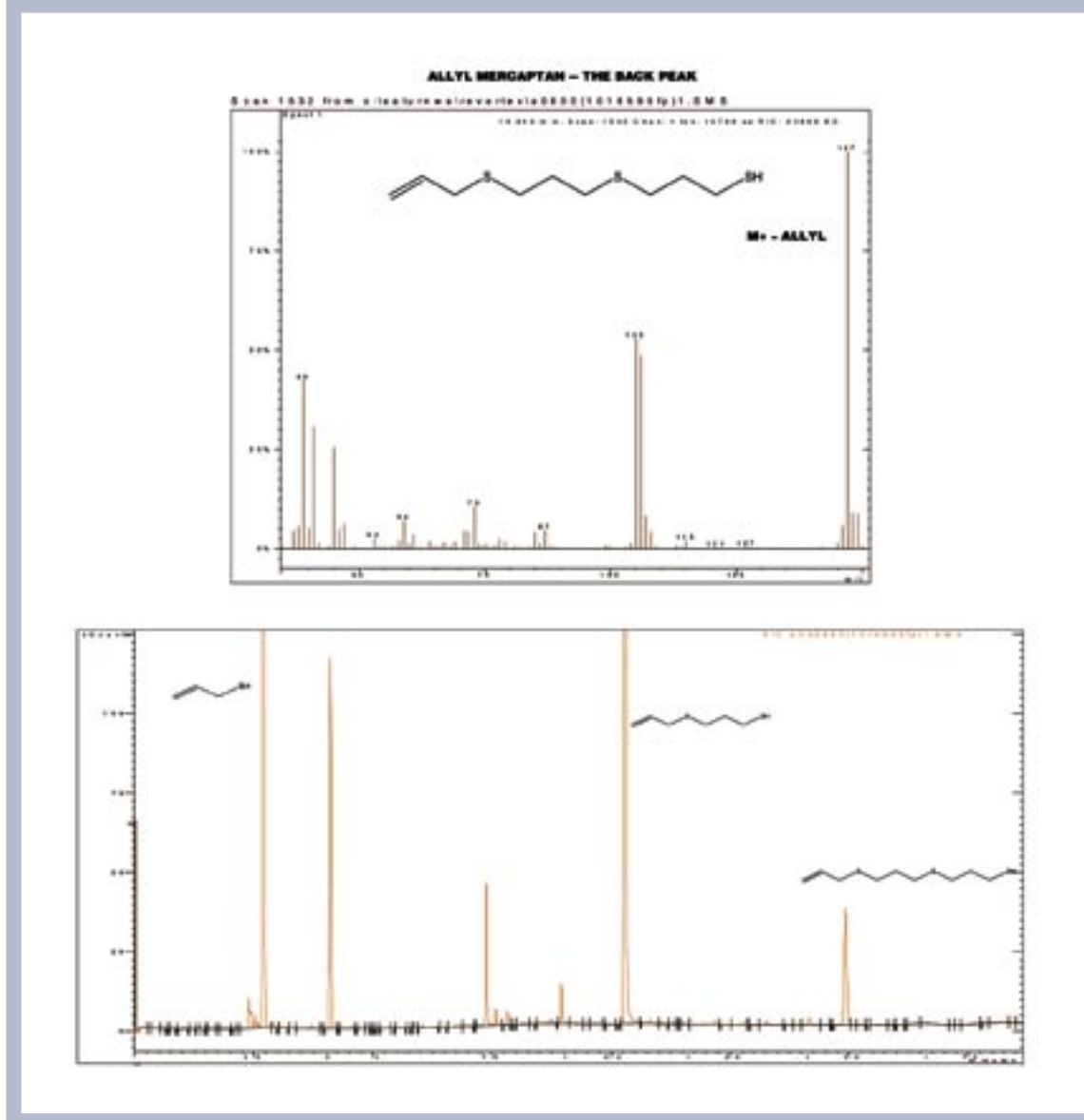
An idea of the range of sulfides can be seen in F-17. The simplest, methyl sul-



fide, is an example of a “symmetrical” sulfide where both substituents on the sulfur are the same; methyl propyl sulfide would be an example of an “asymmetrical” molecule. Sulfides are generally less odorous than mercaptans, but have the advantage of greater chemical stability. The sulfide function is unaffected by acid or base, and is not readily oxidized under conditions that would rapidly convert a mercaptan to a disulfide. This can give us a greater range of potential applications, and this again shows in fragrance applications, using the “tropical” molecule 2-methyl-4-propyl-1,3-oxathiane (F-18).

Here the material shows some useful effects except under the harshest of conditions. While sulfides are much less reactive than mercaptans, they are still oxidized by bleach; hypochlorite can oxidize sulfides to sulfoxides and sulfones (F-19).⁴

In using 2-methyl-4-propyl-1,3-oxathiane as an example, a more pedantic chemist might point out that it is not a simple sulfide, but might be better termed a monothioacetal. This is correct, but the term might lead to an assumption that such a molecule behaves in a similar manner to an oxygen acetal, especially with respect to hydrolysis. That this is not the case is implied by the fragrance studies; under the aqueous acidic conditions that 2-methyl-4-propyl-1,3-oxathiane clearly survives, acetals would be hydrolyzed. We were also able to show this under forcing conditions in the laboratory. When 2-methyl-4-propyl-1,3-oxathiane was boiled with aqueous acid in the presence of a phase transfer catalyst, we observed less than 20



percent hydrolysis to the mercaptoalcohol (F-20).

Di- and Tri-sulfides

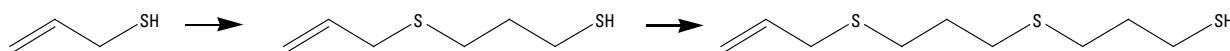
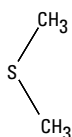
Some important di- and tri-sulfides are shown in F-21. Molecules with this functionality resemble (mono) sulfides in that they are “neutral” and quite resistant to oxidation, but we now have a complication in that they have the weak sulfur-sulfur bond. While this does not have the dangerous instability of the oxygen-oxygen (peroxide) link, it is one of the weakest covalent bonds encountered in organic chemistry (F-22).

It is also a reactive group in that it can be attacked by nucleophiles (F-23).

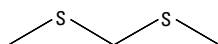
This combination of factors leads to

the most common type of breakdown associated with higher sulfides, a “rearrangement” involving dissociation and recombination. This will not lead to any observed changes when a “symmetrical” disulfide is involved, but with “mixed” disulfides, we see the formation of mixtures, essentially a “statistical” mix of the symmetrical and asymmetrical disulfides (F-24).

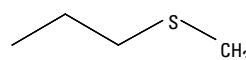
We can see this in the example presented in F-25. Methyl propyl disulfide was shaken with 10 percent aqueous potassium carbonate. In less than 24 h, as a two-phase system at room temperature, the mixture changed from its initial proportions of 96 percent methyl propyl disulfide with 1 percent dimethyl disulfide and 2 percent dipropyl disulfide to 67 percent methyl propyl disulfide with 8 percent dimethyl disulfide and 24 percent dipropyl disulfide (F-25). The deviation from the “theoretical” proportions, based on relative molecular weights, of 50 percent methyl

METHYL SULFIDE (DIMETHYL
SULFIDE, DMS)

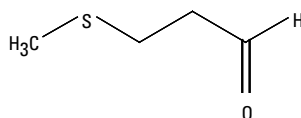
BIS(METHYLTHIO)METHANE [2,4-DITHIAPENTANE]



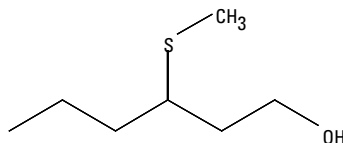
METHYL PROPYL SULFIDE



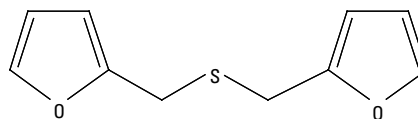
METHIONAL



3-(METHYLTHIO)HEXANOL



THIODIMETHYLENEDIFURAN



propyl disulfide with 19 percent dimethyl disulfide and 31 percent dipropyl disulfide may reflect non-achievement of equilibrium (though little further change took place after shaking for several days) or the response factors on the FID.

With trisulfides we see “disproportionation,” i.e. formation of di- and tetra-sulfides, which takes place whether the sulfide is “symmetrical” or “mixed” (F-26); with a “mixed” trisulfide the resulting mixtures are complex indeed!

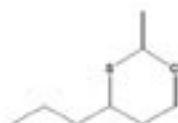
Thioesters

To be more chemically precise, these are S-alkyl thioesters, as in F-27. S-Methyl compounds are the commonest, i.e. derivatives of methyl mercaptan, especially in flavors, though other molecules such as 2-methyl-3-furanthiol acetate (MFT acetate) are known, and there are a number of thioesters found in galbanum oil, such as the derivative of sec-butyl mercaptan shown above. The key “problem” reaction associated with using thioesters is hydrolysis, and, since the mercaptide ion (R-S⁻) is a better leaving group than the alkoxide ion (R-O⁻), thioesters can hydrolyze

more rapidly than “oxygen” esters (F-28).

Since mercaptans are generally more odorous than thioesters, this can be a particular problem. However, we may be able to turn this to our advantage by using thioesters to generate mercaptans *in situ*. The tendency of MFT to oxidize has already been noted, and it is also known to be unstable in aqueous process flavors, so a system that generates this may have advantages for applications.⁵ An enzymatic system for carrying this out has been studied (F-29).⁶

We have found, however, that the enzyme may not be necessary, in that the conditions used in flavor formulations may be sufficient to release the thiol. This was noted during a visit to customers in upstate New York in April 2002. This corresponded to an unseasonable heatwave in the eastern United States; a sample of MFT Acetate in PG in our car was subjected to tempera-

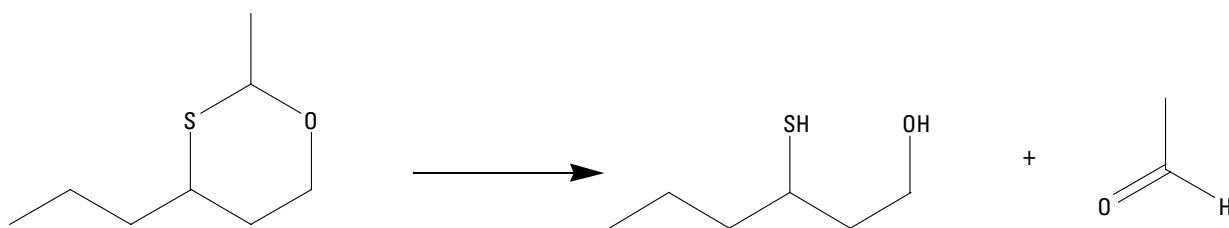
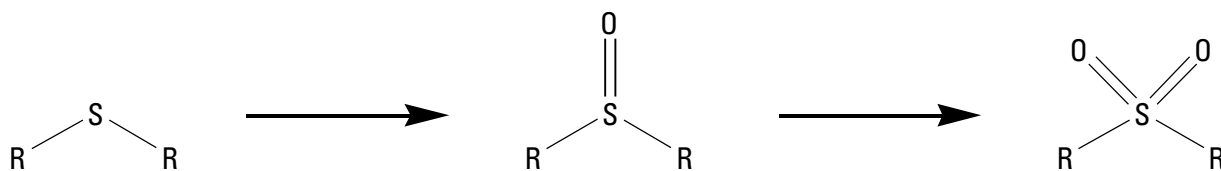


TROPATHANE

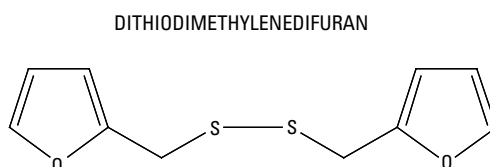
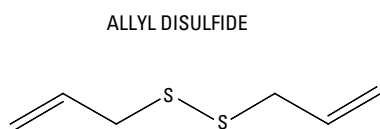
Application	pH	Dilution	WW	BC	Odor at 4°C	Odor at 25°C	Odor at 40°C	Odor at 25°C Daylight	Color at 40°C	Color at 40°C Daylight	Comments	Final Judgement
ACID CLEANER	1	1.0% in DPG	1	0	M	M	M	M	G	G	Weak	M
CREAM RINSE	3.5	1.0% in DPG	0.3	2	G	G	G	G	G	G	Too Strong Woody Fruity Pine	G
TOILET CLEANER	4	1.0% in DPG	0.2	2	G	G	M	G	G	G	Fair	M
DEO STICK	4.3	1.0% in DPG	1	1	G	G	G	G	G	G	Mild OK to Use	G
FABRIC SOFTENER	4.5	1.0% in DPG	0.3	1	G	G	G	M	G	G	Mild Woody	M
DEO PUMP SPRAY	6.6	1.0% in DPG	1	1	G	G	G	G	G	G	Mild Woody	G
EAU DE TOILETTE 85%	7.1	1.0% in DPG	5	2	G	G	G	G	G	G	Woody Fruity Green	G
HAND CREAM	7.5	1.0% in DPG	0.5	0.5	G	G	G	G	G	G	Woody Fruity Green	G

TROPATHANE

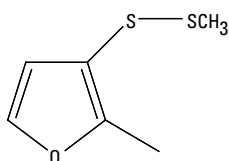
Application	pH	Dilution	WW	BC	Odor at 4°C	Odor at 25°C	Odor at 40°C	Odor at 25°C Daylight	Color at 40°C	Color at 40°C Daylight	Comments	Final Judgement
LIQUID DETERGENT	7.8	1.0% in DPG	0.4	0.5	G	G	G	G	G	M	Good Fruity	M
SHAMPOO	8.3	1.0% in DPG	0.5	0.5	G	G	G	G	G	G	Good	G
TALC	9.7	1.0% in DPG	1	2	G	G	G	G	G	G	Good Very Strong Wood	G
BAR SOAP	10.2	1.0% in DPG	1.5	2	G	G	G	G	G	G	Slightly Weak	G
ALL PURPOSE CLEANER	10.4	1.0% in DPG	0.2	0.5	G	G	G	G	G	G	Woody Good	G
DETERGENT POWDER	10.9	1.0% in DPG	0.2	1	G	G	G	G	G	G	Off	G
COMPACT DET. POWDER	11	1.0% in DPG	0.4	2	G	G	G	M	G	G	Off	G
LIQUID BLEACH	11	1.0% in DPG	0.2	0.5	M	G	G	G	G	M	Off	G



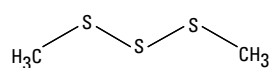
REFLUXING AQUEOUS ACID / PHASE TRANSFER CATALYST
<20% HYDROLYSIS



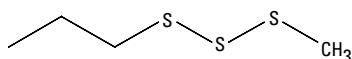
METHYL 2-METHYL-3-FURYL
DISULFIDE



DIMETHYL TRISULFIDE



METHYL PROPYL TRISULFIDE



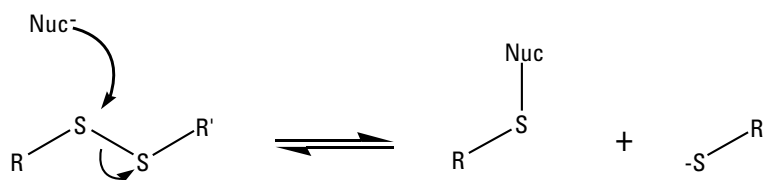
Bond energies in
aroma chemicals

F-22

S—S	222	kJmol ⁻¹
C—C	342	kJmol ⁻¹
C—S	268	kJmol ⁻¹
C—Br	280	kJmol ⁻¹
C—O	352	kJmol ⁻¹

Characteristic chemistry of the disulfide bond

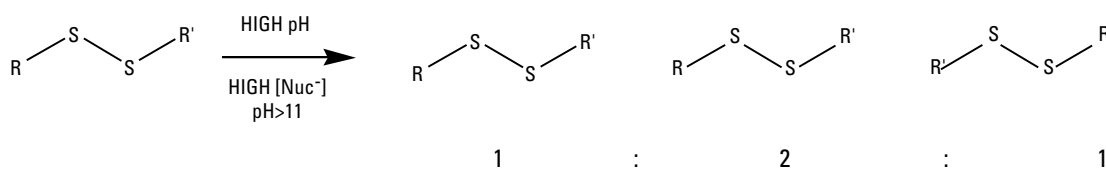
F-23



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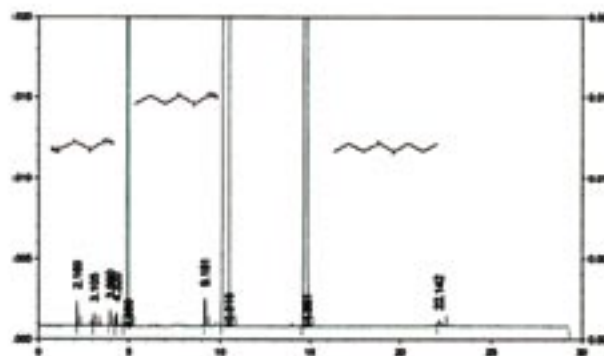
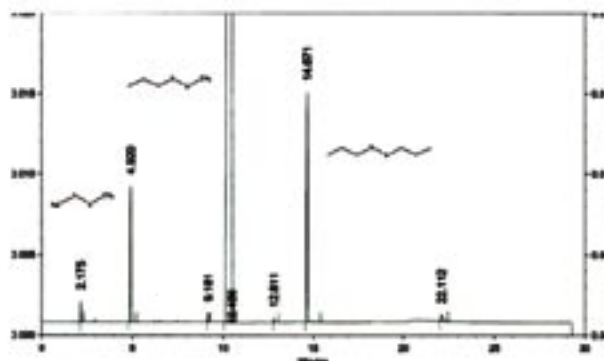
“Rearrangement” of a mixed disulfide

F-24



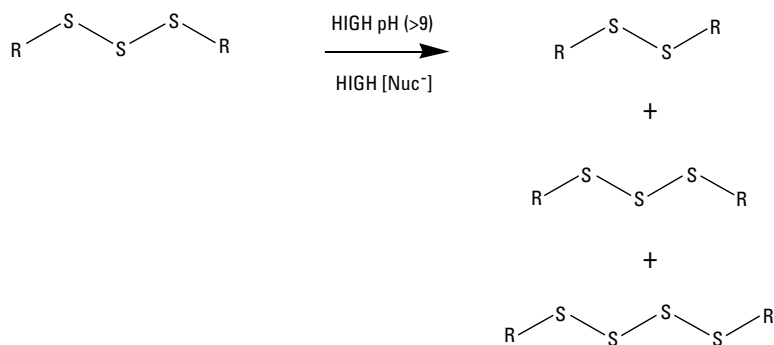
“Rearrangement” of methyl propyl disulfide

F-25



"Disproportionation" of a trisulfide

F-26

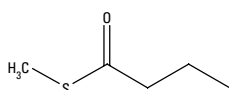


15

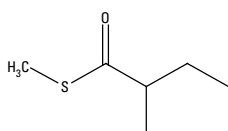
Some important thioesters

F-27

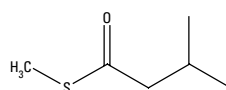
METHYL THIOBUTYRATE



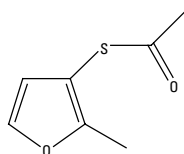
METHYL (2-METHYL)THIOBUTYRATE



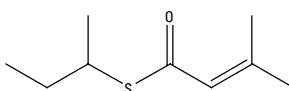
METHYL (3-METHYL)THIOBUTYRATE



2-METHYL-3-FURANTHIOL ACETATE

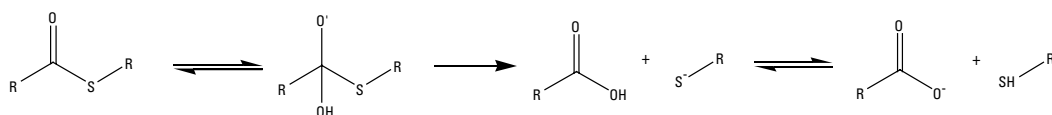


sec-BUTYL 3-METHBUT-2-ENETHIOATE



"Disproportionation" of a trisulfide

F-28



MFT acetate as an in situ precursor of MFT **F-29**



A POTENTIAL SLOW RELEASE SYSTEM FOR MFT

ENZYMATIC HYDROLYSIS

C. rugosa LIPASE

An accidental discovery **F-30**



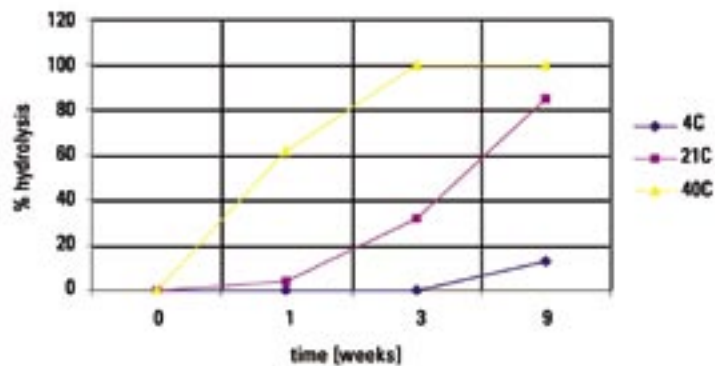
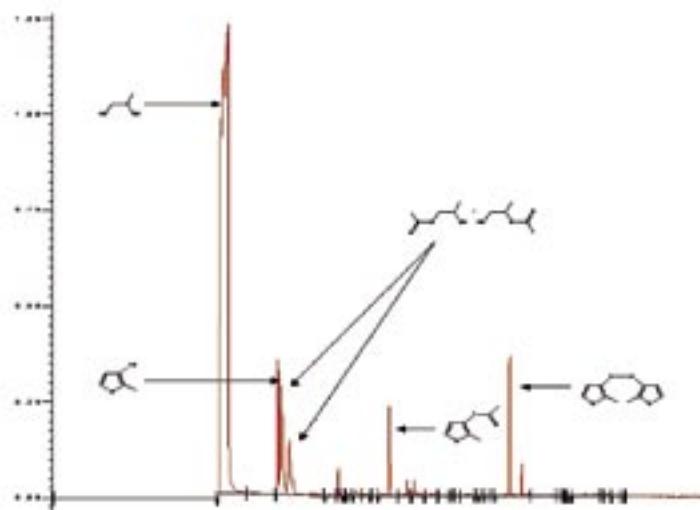
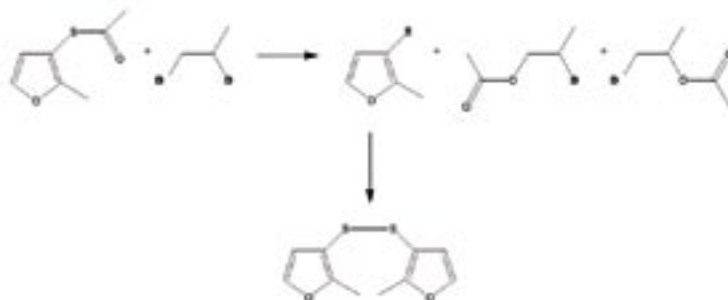
A POTENTIAL SLOW RELEASE SYSTEM FOR MFT

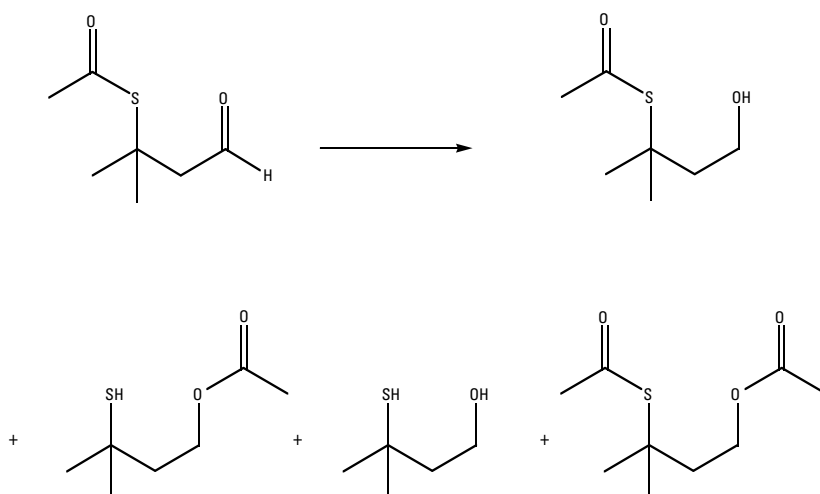
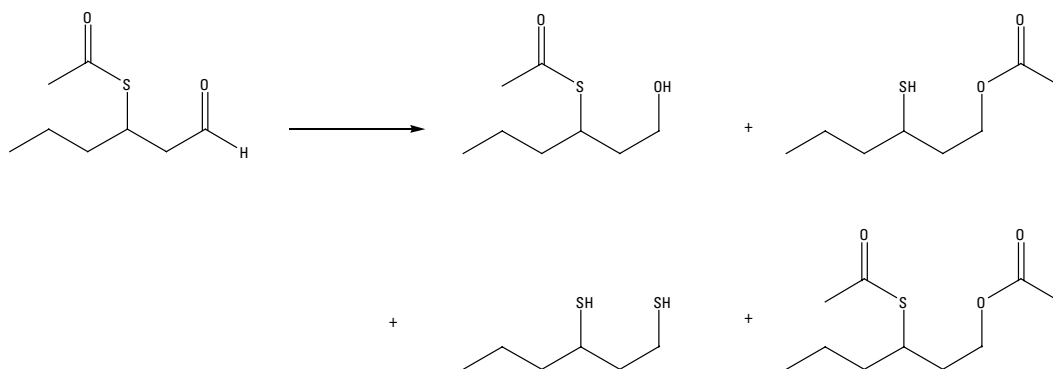
NON-ENZYMATIC HYDROLYSIS

1. IN PG, HEATED IN A CAR IN UPSTATE NEW YORK IN A SPRING HEATWAVE!
2. IN PG, CONTROLLED CONDITIONS

16

The alcoholysis of MFT acetate **F-31**





tures that were certainly excessive for the human occupants. It was very clear that hydrolysis (or, more strictly, alcoholysis) had taken place, because the odor was much stronger than expected. A sample that had been carefully prepared to show the character of the material but not to be so strong as to wipe out the nose of the customer was now overpowering (F-30)!

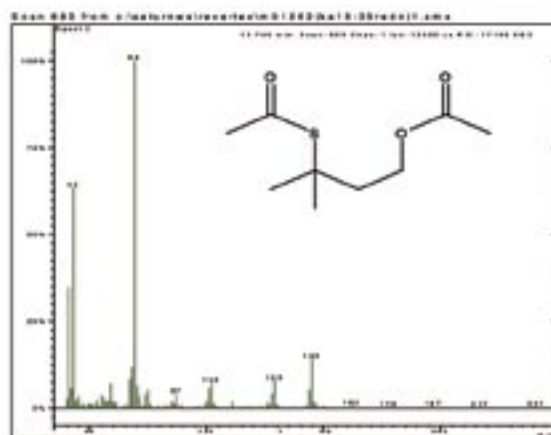
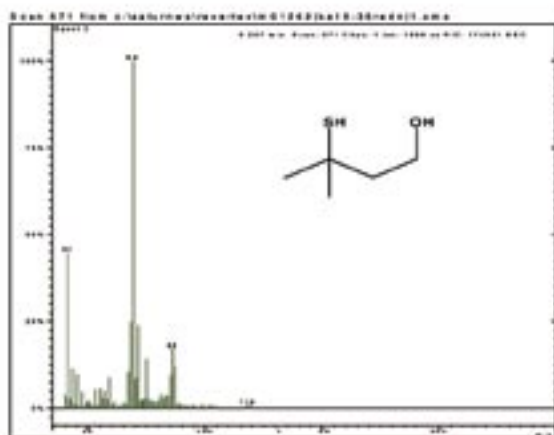
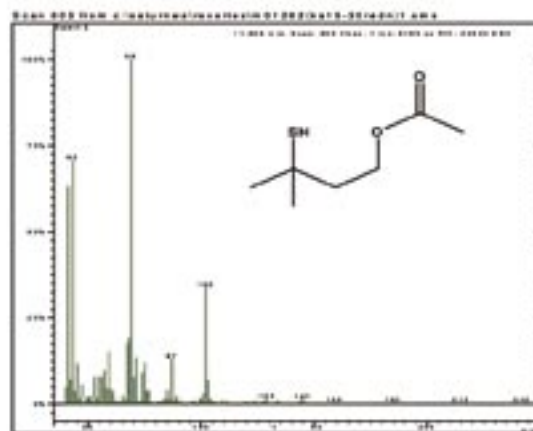
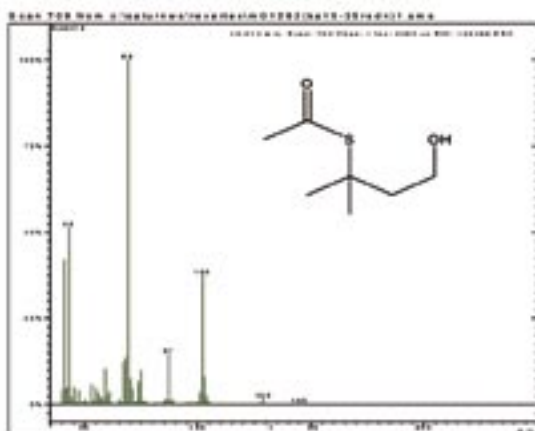
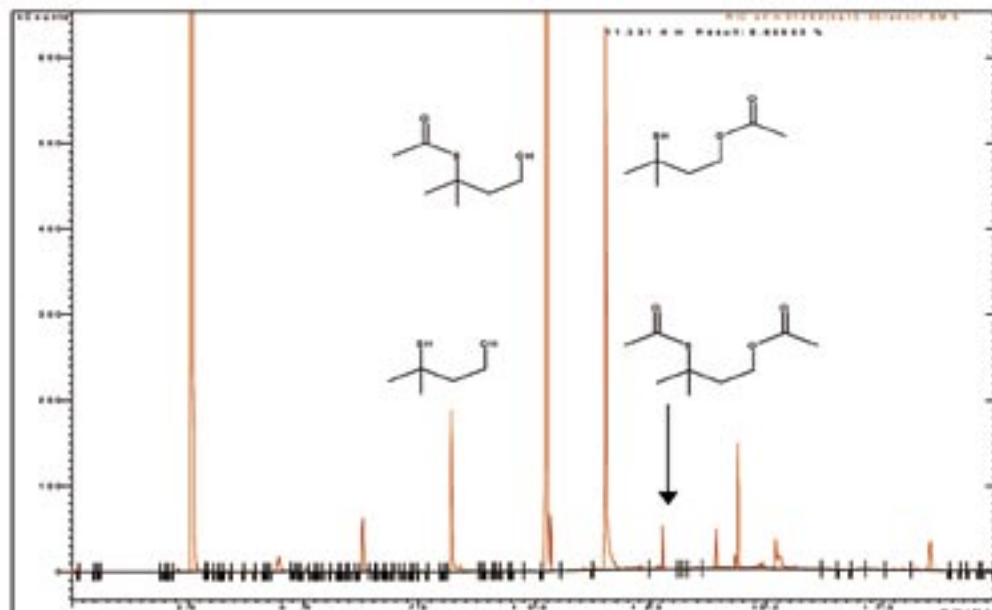
On this basis, we decided to look at the reaction under controlled conditions, i.e. the reaction of a 10 percent solution in PG at 4°C (refrigerator), 21°C (ambient) and 40°C (accelerated aging). We were able to detect all the components, including the acetates of PG formed in the reaction, and in the older samples, bis (2-methyl-3-furyl)

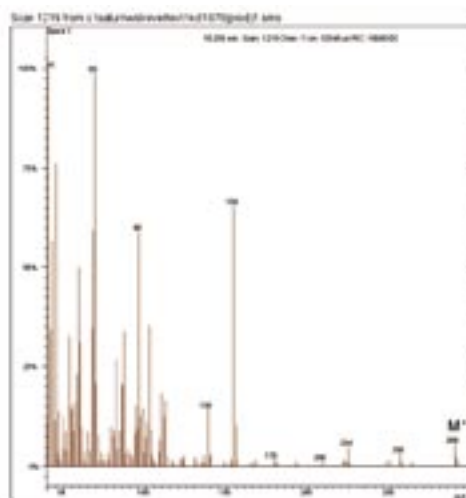
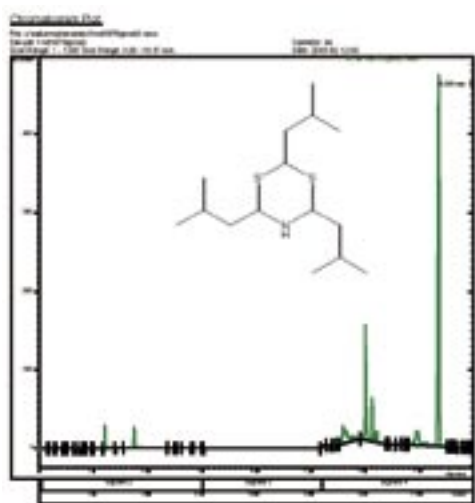
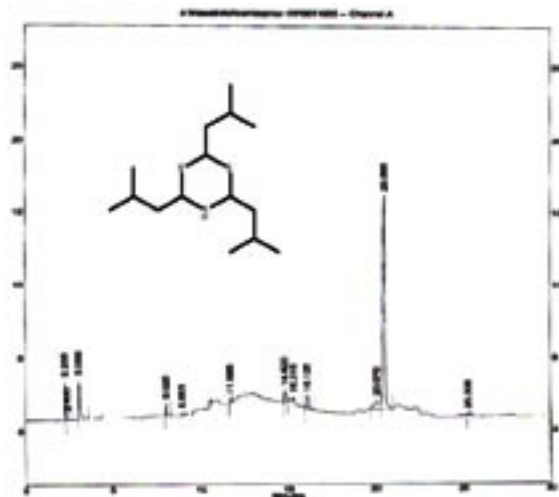
disulfide formed by oxidation of the liberated MFT (F-31). We can see from this that over the typical shelf life of a formulation, extensive MFT formation will take place. With care, it may be possible to develop a “steady-state” concentration of mercaptan, where any losses due to oxidation are balanced by generation from the acetate.

The hydrolysis is, of course, reversible, in that a mercaptan can react with an ester to generate a thioester and an alcohol. We see this in the “OAc-SAc shuffle,” the intramolecular reaction where a mercaptan and an ester in a 1,3-relationship interact, as shown in the reduction of 3-(acetylthio) hexanal (F-32).

We recently came across another example in the reduction of 3-(acetylthio)-3-methylbutanal (F-33).

Two main peaks were observed, which had es-





entially identical mass spectra, and are believed to be the mercaptan/acetate and the alcohol/thioacetate. Neither shows a molecular ion (m/z 162), but both show loss of acetic acid ($M^+ - 60 = m/z$ 102), loss of the thioacetyl group ($M^+ - 75 = m/z$ 87) as well as complete fragmentation to the stable isoprenyl ion (m/z 69). The identical nature of both mass spectra, and most importantly, that the spectra show characteristics of both an acetate and a thioacetate in the same molecule, indicates that

the OAc/Sac shuffle is also taking place in the mass spectrometer. The other two peaks are the diacetate and the mercaptoalcohol, presumably formed by intermolecular transacylation (F-34).

Dithiazines

Two recent FEMA GRAS dithiazines are shown in F-35. Materials of this type are commonly found in “bacon” type reaction flavors formed by the reaction of aldehydes with ammonia and hydrogen sulfide. A key question is as to whether they are actually naturally occurring. While we cannot answer that question,

we can show the problems with identifying them in foodstuffs. 2,4,6-Triisobutylidithiazine is a crystalline compound with a sharp melting point. However, we were unable ever to get a good GC by any standard method. We got a distinct peak, but a broad hump dominated the chromatogram, presumably due to breakdown. GC/MS confirmed that the defined peak was the dithiazine, but breakdown still occurred; the GC/MS trace looks better than the standard GC only because we had to turn off the detector during the hump as the number of peaks being detected overloaded the data collection system (F-36).

This illustrates the potential difficulties associated with analysis of these materials. If analysis of a sample of pure, crystalline, synthetic material is so difficult, then the identification of trace quantities of dithiazines in the complex mixtures found in the real world will be orders of magnitude more problematic.

Conclusions

The wide range of potential application for sulfur compounds makes them essential components of a perfumer or flavorist's tool kit. Sulfur chemicals are still being introduced to the industry, and at a rate disproportionately large compared to other groups of molecules. The reactivity of sulfur chemicals must be taken into account when considering the usage of these materials, but it may even be possible to turn that reactivity to the advantage of the user.

Acknowledgements

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