# Synthesis and Aroma Properties of Bis 1,1 and 2,2 (Methylthio) Alkanes

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**SUMMARY**—In this study, we investigated the preparation and organoleptic properties of two series of bis-methylthio compounds. The reactants are either the homologous series of n-alkanals or methyl n-ketones and methyl mercaptan. The reactions proceed cleanly to produce the desired products. The character of the products is distinctly different from the reactants. The lower members possess green and sulfurous aromas. The intermediate chain length compounds are sharp and fruity while the high molecular weight products are generally like cooked (sulfury) vegetables.

Aliphatic carbonyl compounds can be found in the volatile essence of most foods.[1] Similarly, methylmercaptan is a predominant sulfur-containing odorant in many foods such as coffee,[2] meat,[3] and milk.[4] Since aliphatic carbonyls and methyl mercaptan possess interesting flavor notes in themselves, we investigated the organoleptic properties of the compounds formed by the reaction of figure 1 or, in the more general case herein studied of figure 2.

Bis (methylthio) methane has been reported to occur in boiled beef[3] as well as in cheese,[5] and bis (methylthio) ethane has been reported in beef.[6] These occurrences provided additional impetus to study this series of flavorants.

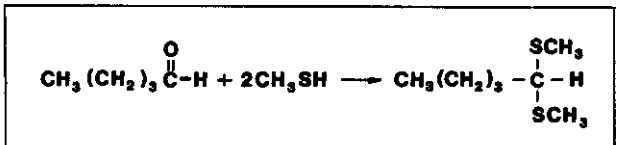


**Figure 1**

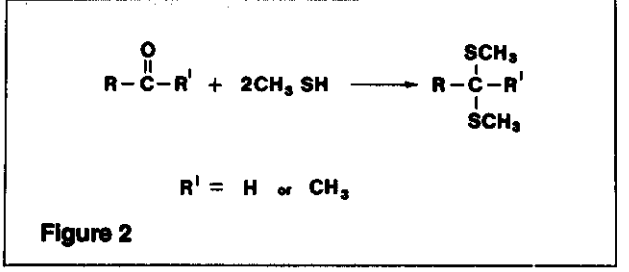


**Figure 2**


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## Experimental—General Synthesis

To a round-bottom flask fitted with a magnetic stirrer and ice water bath is added 10 ml of methylene chloride, 2 ml of starting aldehyde or ketone, and a small quantity of molecular sieve to remove water formed during the reaction. To this stirred solution is added 4 ml of methyl mercaptan and (cautiously) 0.2 ml of $BF_3$ etherate. The mixture is allowed to stir at room temperature for 4 hours. Finally, the reaction is washed with saturated NaCl solution, dried over $NaSO_4$, and purified by preparative scale gas chromatography (SP-2100). The purified products were analyzed by IR and GC/MS as proof of their identity. Representative spectral information is indicated for 1,1 bis (methylthio) hexane. Infrared spectra indicated loss of all carbonyl (1730 cm-1) and aldehydic protons (2830, 2720 cm-1). Mass spectral analysis shows loss of methylthio groups and typical n-alkyl fragmentation patterns.

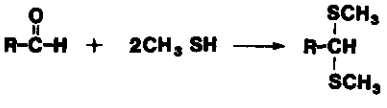
## Results

The homologous series of 1, 1 bis (methylthio) alkanes from $C_3$ to $C_{12}$ was synthesized by reacting the appropriate n-aldehyde with methyl mercaptan. In a similar fashion, the homologous series of 2,2 bis (methylthio) alkanes was synthesized using the appropriate methyl n-alkyl ketone. (To our knowledge, these compounds have not been previously evaluated by organoleptic methods.) The reaction mixtures were purified via gas chromatography and structural characterization was obtained using infrared and gas chromatographic/mass spectral analysis. Organoleptic properties of the synthesized compounds were obtained using a "sip and spit" protocol on serial dilutions of the pure products. These characterizations were made by members of our Natural Products Group. The character of the members of the $C_1$ bis (methylthio) alkane series is given in Table I, along with the thresholds in spring water (w/w).

The lower members of this series had gaseous and sulfurous aromas. The medium chain length alkyl homologues were found to possess some green character as well as a grapefruit rind-citrus note. The higher homologues were found to have an oily/cooked vegetable character with sulfurous overtones. The most notable members of this series are 1,1 bis (methylthio) pentane and 1,1 bis (methylthio) hexane, which have green/grapefruit-citrus notes.

**Table I. 1, 1 Bis (Methylthio) Alkanes**

**1,1-BIS (METHYLTHIO) ALKANES**

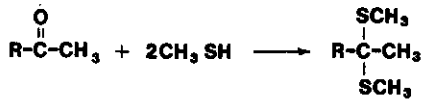


| Reactant | | Product | | |
|---|---|---|---|---|
| Aldehyde | Character (7) | R= | Threshold (ppm) | Evaluation |
| Propanal | sweet, ethereal green | $CH_3CH_2$ | 0.05 | green/gaseous/sulfurous |
| Butanal | green-fresh fruity, irritating | $CH_3(CH_2)_2$ | 0.05 | green/gaseous/vegetable |
| Pentanal | dry fruity, musty, nut-like | $CH_3(CH_2)_3$ | 0.06 | green/sulfurous/grapefruit |
| Hexanal | fatty-green, grassy | $CH_3(CH_2)_4$ | 0.1-0.3 | green/grapefruit-citrus/sulfurous |
| Heptanal | oily-fatty, "rancid," fermented | $CH_3(CH_2)_5$ | 0.1-0.3 | grapefruit-citrus/spicy/sweet |
| Octanal | sweet, orange, sl. fatty | $CH_3(CH_2)_6$ | 0.1-0.3 | green/broccoli/soapy/fatty |
| Nonanal | floral, waxy, fatty, rosy | $CH_3(CH_2)_7$ | 0.4-4.0 | fatty/fried vegetable/green |
| Decanal | sweet waxy, orange peel | $CH_3(CH_2)_8$ | 0.5-5.0 | sulfurous vegetable/rubbery |
| Undecanal | waxy floral | $CH_3(CH_2)_9$ | 10 | strong sulfur vegetable/boiled onion |
| Dodecanal | sweet, waxy-herbaceous, floral | $CH_3(CH_2)_{10}$ | 10 | garlic flash/sulfurous vegetable |

**Table II. 2, 2 Bis (Methylthio) Alkanes**

| Reactant | | Product | | |
|---|---|---|---|---|
| Ketone | Character (7) | R= | Threshold (ppm) | Evaluation |
| Acetone | ethereal/sweet-burning | $CH_3$ | 0.2 | green/sharp/olefinic |
| 2-Butanone | ethereal | $Ch_3CH_2$ | 0.2 | green/sharp/sulfurous |
| 2-Pentanone | sweet/ethereal-fruity/ banana | $CH_3(CH_2)_2$ | 0.4 | green/resinous/sulfurous vegetable |
| 2-Hexanone | fruity/sweet | $CH_3(CH_2)_3$ | 1.0-3.0 | green/fruity/grapefruit |
| 2-Heptanone | spicy/fruity | $CH_3(CH_2)_4$ | 1.5-4.5 | green/fruity/peachy |
| 2-Octanone | pleasant/floral/bitter-green slightly musty-herbaceous | $CH_3(CH_2)_5$ | 5-10 | cedar/dill/green/sulfur |
| 2-Nonanone | fruity-floral/slightly fatty-herbaceous | $CH_3(CH_2)_6$ | 5-10 | fatty/green/cooked vegetable |

**2,2—BIS (METHYLTHIO) ALKANES**



The difference in character between the starting alkanal and the reaction product is quite striking. For example, hexanal has a fatty-green, grassy note, while the reaction product is grapefruit/citrus.

Table II contains the organoleptic properties of the $C_2$ bis (methylthio) alkanes, as well as their respective thresholds. Organoleptic properties of the $C_2$ series show good correlation with the $C_1$ series of bis (methylthio) alkanes when total carbon number is compared. For example, both 1,1 bis methylthio and 2,2 bis methylthio hexane have a grapefruit character. The aromas of the $C_2$ substituted alkanes progress from green and sharp through green/fruit-like to fatty, cooked vegetable as chain length increases. The most interesting members of this series are 2,2 bis (methylthio) hexane (grapefruit-citrus) and 2,2 bis (methylthio) heptane (fruity peach-like).

Again, it is instructive to note the distinct change in character effected by reaction with 2 moles of methyl mercaptan. 2-Heptanone is reminiscent of blue cheese; its reaction product loses this character to become fruity and peachy.

## Discussion

Isolation and identification of aroma chemicals from natural materials can be quite time consuming. It frequently requires the work-up of tens or hundreds of kilograms of sample. This effort frequently yields only micrograms of purified aroma chemical to be used for both structural elucidation and aroma characterization. Finally, chemical synthesis is needed to prove the structure in an unequivocal fashion. On the other hand, if we can postulate the reactions that lead to flavor compounds, we can go directly to the third step—that of synthesis. This may lead to a more efficient search process, limited only by our imagination and creativity.

In the current study, we synthesized two series of bis (methylthio) compounds that have not been described in the flavor literature before. The character is distinctly different from that of the reactants, and some interesting fruity and vegetable aromas were obtained.

### References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