

Flavor compounds

Meaty Aromas, Part II

Syntheses and odor characteristics of 1-alkylthio-2-butanethiols, 1-alkylthio-2-butanols and their derivatives

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We previously have proposed a presumption that most meaty flavor compounds have a common characteristic structural unit that contains sulfur or oxygen heteroatoms on the adjacent two carbon atoms (one of the heteroatoms should be a sulfur atom). This characteristic structural unit can be further classified into six subclasses (F-1) according to different bonding forms.¹⁻² In order to verify our presumption, four series of compounds were synthesized in our lab, including 1-alkylthio-2-butanethiols, 1-alkylthio-2-butanols, 2-methoxy butyl alkyl sulfides and 1-alkylthio-2-butanones. They have the characteristic structural unit a, b and e individually, as shown in F-1. The odor characteristics of these compounds were evaluated by flavorists.

Compounds

1-Alkylthio-2-butanethiols were synthesized by the reactions of thiols and 1,2-epithiobutane that were prepared through 1,2-epoxybutane and thiourea.³⁻⁴ The nucleophilic substitution reactions of thiols with 1,2-epithiobutane gave moderate yields of 40–50 percent. Some residuals with high boiling points remained after the desired products were distilled out. The poor yields may be due to self-polymerization of 1,2-epithiobutane and/or the further reactions of products with 1,2-epithiobutane.

1-Alkylthio-2-butanols were synthesized directly by the reactions of thiols with 1,2-epoxybutane. This reaction went

well with yields of more than 70 percent. In order to study the effects of functional groups on compound aromas, the hydroxyl groups of 1-alkylthio-2-butanols were transformed into methoxy groups by reactions with iodomethane in the presence of sodium hydride. Through Swern oxidation, 1-alkylthio-2-butanols were transformed into 1-alkylthio-2-butanones with high yields of 80–90 percent.⁵

The solutions (w/w = 1 percent) of these four series of compounds were made by dissolving them in 1,2-propanediol. The aroma evaluations were carried out by using these solutions. The results are listed in T-1 through T-4.

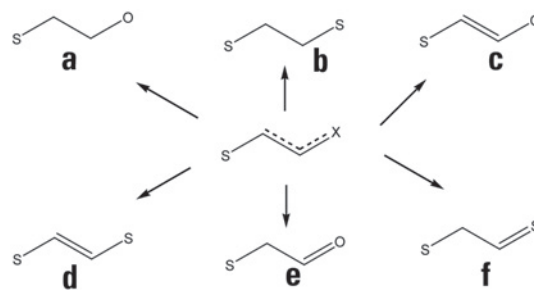


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Hongyu Tian et al. published their initial study on compounds with meat flavors in the January/February 2005 issue of *Perfumer & Flavorist* magazine (*Meaty Aromas*, page 36). In it, the authors describe the characteristic structural unit of sulfur-containing compounds with a basic meat flavor. You can purchase this article through the *P&F* magazine Article Archives at www.perfumerflavorist.com/articles.

Six subclasses of sulfur-containing compounds with a meat flavor; X=S or O

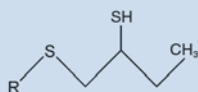
F-1



Odor characteristics of 1-alkylthio-2-butanethiols

T-1

Compounds



R = ethyl

R = propyl

R = butyl

R = hexyl

R = octyl

R = furfuryl

Odor characteristics

Intensive onion and garlic with a vegetable note

Spearmintlike

Spearmintlike with a melon note

Roasted with a melon note

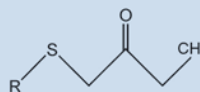
Baked cereal

Baked rice

Odor characteristics of 1-alkylthio-2-butanones

T-4

Compounds



R = ethyl

R = propyl

R = butyl

R = hexyl

R = octyl

R = furfuryl

Odor characteristics

Intensive green radish with an onion and garlic note

Intensive dry radish

Stewed meat, onion and garlic

Stewed meat, rubbery and pickled vegetables

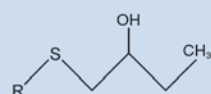
Pickled vegetables with a faint mushroom note

Roasted nut and baked barley

Odor characteristics of 1-alkylthio-2-butanols

T-2

Compounds



R = ethyl

R = propyl

R = butyl

R = hexyl

R = octyl

R = furfuryl

Odor characteristics

Garlic with an onion and vegetable note

Onion with a garlic and green fruit note

Onion with a garlic note

Green fruit with an onion and garlic note

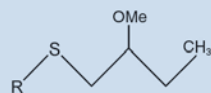
Rubbery with a carvone note

Tropical fruit with a faint onion and garlic note

Odor characteristics of 2-methoxy butyl alkyl sulfides

T-3

Compounds



R = ethyl

R = propyl

R = butyl

R = hexyl

R = octyl

R = furfuryl

Odor characteristics

Green vegetable with a faint onion and garlic note

Sweet radish

Sweet radish with an onion and garlic note

Metallic with a faint onion and garlic note

Boiled vegetable

Fresh and salty with an onion and garlic note

Aroma Evaluations

1-Alkylthio-2-butanethiols have the characteristic structural unit S-C-C-S (see T-1). 1-Ethylthio-2-butanethiol possessed intensive onion and garlic aromas with a weak vegetable note. 1-Propylthio-2-butanethiol had a spearmintlike aroma. 1-Butylthio-2-butanethiol possessed a spearmintlike aroma with a melon note, while 1-hexylthio-2-butanethiol had a roasted aroma with a melon note. 1-Octylthio-2-butanethiol possessed a baked cereal aroma, and 1-furfurylthio-2-butanethiol had a baked rice aroma. The results show that different alkyl groups significantly impact the odor characteristics of compounds. The odor type changed gradually from onion/garlic to baked aromas with the increase of alkyl chains.

1-Alkylthio-2-butanols have the characteristic structural unit S-C-C-O. The results (see T-2) also indicate that the size of alkyl groups affected the compounds' aromas. The onion and garlic aromas weakened gradually, and the fruity aromas strengthened. 1-Furfurylthio-2-butanol possessed a tropical fruit aroma with a faint onion and garlic note.

The hydroxyl groups of 1-alkylthio-2-butanols were transformed into methoxy groups to give 2-methoxy butyl alkyl sulfides that have the same characteristic structural unit S-C-C-O as 1-alkylthio-2-butanols (see T-3). However, the corresponding compounds in these two series have totally different odor characteristics. For example, 1-ethylthio-2-butanol possessed a garlic aroma, while the corresponding 2-methoxy butyl ethyl sulfide

had a green vegetable note. In addition, 1-octylthio-2-butanol possessed a rubbery odor, while 2-methoxy butyl octyl sulfide had a boiled vegetable note.

1-Alkylthio-2-butanones were given through Swern oxidation of 1-alkylthio-2-butanols that have the characteristic structural unit S-C-C=O (see T-4). Among this series of compounds, 1-butylthio-2-butanone and 1-hexylthio-2-butanone possessed a stewed meat aroma. 1-Ethylthio-2-butanone had an intensive green radish aroma with an onion and garlic note, while 1-propylthio-2-butanone had an intensive dry radish aroma. 1-Octylthio-2-butanone possessed a pickled vegetable aroma with a faint mushroom note, and 1-furfurylthio-2-butanone had a roasted nut and baked barley aroma.

Conclusions

Four series of compounds were synthesized starting from 1,2-epoxybutane, including 1-alkylthio-2-butanethiols, 1-alkylthio-2-butanols, 2-methoxy butyl alkyl sulfides and 1-alkylthio-2-butanones. Compounds within the same series presented different aroma types, although they had the common characteristic structural unit. Obviously, different alkyl groups impact the compounds' odor characteristics. For example, 1-alkylthio-2-butanols and 2-methoxy butyl alkyl sulfides had the same characteristic structural unit S-C-C-O, but the corresponding compounds possessed different aromas. Among the

series of 1-alkylthio-2-butanones, 1-butylthio-2-butanone and 1-hexylthio-2-butanone were found to have a stewed meat aroma, which is consistent with our presumption.

We can conclude that functional groups and the size of alkyl chains on the characteristic structural unit have significant effects on the aromas of the compounds. There were two compounds among the 24 that we synthesized that possessed a meaty aroma, as we predicted. These results indicate that our presumption has certain predictability, although with limited accuracy. More research work about this presumption is still ongoing in our lab.

Acknowledgements

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References

1. B. Sun et al., *Jinxihuagong*, **18**(8), 456 (2001).
2. B. Sun, H. Tian, F. Zheng, Y. Liu and J. Xie, *Meaty Aromas*, *Perfum. Flavor.*, **30**(1), 36-45 (2005).
3. F.G. Bordwell et al., *J. Am. Chem. Soc.*, **75**, 4959 (1953).
4. C.C.J. Culvenor et al., *J. Chem. Soc.*, 4480 (1952).
5. M. Marx et al., *J. Org. Chem.*, **49**, 788 (1984).

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