

Aroma Properties of Some Alkylthiazoles

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Thiazoles are a class of compounds possessing a five-membered ring with sulfur and nitrogen in the 1 and 3 positions (figure 1). Although thiazole and its derivatives have been known to organic chemists for a century,¹ their sensory properties were not appreciated until relatively recently. The potential of thiazole derivatives as flavorants became evident through the work of Stoll et al.² who found that the strong nut-like odor of a basic fraction obtained from a cocoa extract was due to a trace amount of 4-methyl-5-vinylthiazole. Since then, numerous thiazoles were identified in food flavors.

The occurrence of thiazoles in food flavor has been reviewed.^{3,4} More recently, thiazoles have been identified in baked potato,^{5,6} roasted peanuts,^{7,9} roasted beef,¹⁰ cocoa butter,¹¹ fried bacon¹² and fried chicken.¹³ Thiazoles have also been reported in various model system reactions involving either degradation of glucose in the presence of hydrogen sulfide and ammonia,^{14,15} or more frequently, fragmentation of cysteine or cystine,¹⁶⁻¹⁸ or reaction of these with xylose,¹⁹ ribose,²⁰ pyruvaldehyde,²¹ furaneol¹⁸ or glucose.²¹

Aroma properties for some alkylthiazoles have been reviewed.^{3,22} The most typical alkylthiazole is probably 2-isobutylthiazole. This compound was isolated from tomato flavor²³ and was described as having a strong green odor resembling that of tomato leaf. When added to canned tomato puree or paste at levels of 20 to 50 ppb, 2-

isobutylthiazole develops an intense fresh tomato-like flavor. Some 4,5-dialkylthiazoles were synthesized and reported to have potent bell pepper-like aroma.²⁴ The flavor threshold value for 4-butyl-5-propylthiazole was judged to be 0.003 ppb in water.²⁴ Most of the alkylthiazoles were described as green, nutty and vegetable-like.²⁵

In this paper, the aroma properties of some synthesized alkylthiazoles are reported.

Experimental

Materials—aliphatic ketones, aliphatic aldehydes, bromine, amide, acids were obtained.

Synthesis of α -Bromo Ketones—These were synthesized by the methods described by Catch et al.,²⁶ which involve essentially direct bromination of the appropriate ketone. With unsymmetrical ketones, two bromoketones are formed.

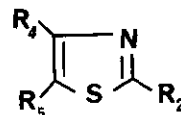


Figure 1. Structure of Alkylthiazole

In all cases, the mixture of the two bromides was taken through the thiazole synthesis and the two isomeric thiazoles were separated by GC.

Synthesis of α -Bromo Aldehydes—These were

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Table I. Aroma Qualities of Synthetic Alkylthiazoles

<u>Alkylthiazoles</u>	<u>Occurrence in Food</u>	<u>Aroma Description</u>
2-isopropyl-4-methylthiazole	cocoa butter (11)	strong camphor-like, sassafras-like, nutty
5-pentylthiazole		strong, fatty, sweet, bacony, long-lasting
2-pentylthiazole	cocoa butter (11)	strong, green, fatty, sweet, raw nutty, mushroom-like
2-propyl-4-ethyl-5-methylthiazole	roasted beef (10)	rubbery, minty, spicy
2-isopropyl-4-methyl-5-ethylthiazole		raw sweet potato-like
2-pentyl-5-methylthiazole		vegetable, leek-like, fermented vegetable, long-lasting
2-pentyl-4-methylthiazole	roasted beef (10)	strong, green, vegetable, slightly meaty
2,4-dimethyl-5-pentylthiazole		strong flowery, fruity, sweet sulfury background
2,4-diethyl-5-propylthiazole		strong, papaya-like, mango-like
2-ethyl-4-butyl-5-methylthiazole		strong, sulfury, spicy
2-butyl-4-methyl-5-ethylthiazole	roasted beef (10) fried chicken (13)	green, pleasant, vegetable green note
2-butyl-4-propylthiazole		sweet, flowery, herbal
2-pentyl-4-ethylthiazole		very sweet, nutty
2,5-diethyl-4-propylthiazole		fruity, mango-like, papaya-like
2-pentyl-4-methyl-5-ethylthiazole		strong green pepper (paprika type)
2-pentyl-4-propylthiazole		nutty, roasted, caramel, slightly sweet
2-hexyl-4-ethylthiazole		sweet, slightly fatty
2-heptyl-4,5-dimethylthiazole	fried chicken (13)	very strong spicy, sulfury
2-heptyl-4-ethylthiazole		burnt nutty, green
2-heptyl-4-ethyl-5-methylthiazole	fried chicken (13)	sweet, fruity, fatty, coconut-like
2-octyl-4,5-dimethylthiazole	fried chicken (13)	weak, slightly sweet, fatty
2-octyl-4-ethylthiazole		very weak, rubbery
2-octyl-4-propylthiazole		very weak, rubbery

synthesized by the method of Bedoukian,²⁷ which involved conversion of the corresponding saturated aldehyde to its enol acetate followed by the addition of bromine and then conversion to the dimethyl acetal and hydrolysis to the α -bromo aldehyde.

Synthesis of Alkylthiazoles—The alkylthiazoles were synthesized using the method of

Kurkcy and Brown.²⁸ This involves addition of the α -bromoketone or α -bromoaldehyde to the pre-formed thioamide. Yields were satisfactory at about 50% and the distilled products were purified by GC. Gas chromatography was performed on a Beckman GC-55 gas chromatograph, fitted with a 12 ft. long x $\frac{1}{8}$ in. o.d. stainless steel column packed with 10% SP-1000 on 80/100-

mesh Chromosorb W. The flow rate was 30 ml/min. The column temperature was programmed from 50° to 230°C at a rate of 5°C/min. The purified alkylthiazoles were subjected to aroma evaluation.

Results and Discussion

The aroma qualities of the alkylthiazoles synthesized were described by a panel of three experienced flavorists and are listed in Table I.

Significant flavor correspondence between the thiazoles and derivatives of pyridines and pyrazines possessing comparable functional groups has been reported by Pittet and Hruza.²⁵ They stated that the low 2-alkylthiazoles have green, vegetable-like flavors. Corresponding monoalkylpyridines, too, have a green odor.²⁵ In this study, 2-pentylthiazole was judged to have green, fatty and sweet aromas. This does have some similarity with corresponding 2-pentylpyridine which was reported to have fatty and tallowy odors.

Thiazoles and oxazoles possessing comparable alkyl groups were found to have significant aroma similarities. Buttery et al. reported that some 4,5-dialkylthiazoles possessed potent bell pepper aroma.²⁴ The most potent one, 4-butyl-5-propylthiazole, was reported to have the flavor threshold of 0.003 ppb in water. Ho and Tuorto synthesized several 4,5-dialkyloxazoles and found them to have a green, vegetable-like aroma.³⁰ 4-Butyl-3-propyloxazole was evaluated to have a strong bell pepper aroma with a flavor threshold of 0.1 ppm in water.³¹ In this work, several thiazoles were also found to have similar aroma characteristics with corresponding oxazoles. 5-Pentylthiazole had strong fatty and sweet aromas reminiscent of that of bacon fat, and the corresponding 5-pentyloxazole was reported to be green and bacon-fatty. 2-Pentyl-5-methylthiazole was judged to have fermented vegetable-like aroma, and the corresponding 2-pentyl-5-methyloxazole was described as acidic, fatty, sweet and having a flowering after-note.

The wide range of aroma characteristics of these alkylthiazoles suggests that they may be of greater use in processed foods or perfume application.

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