

Aroma Properties of Some Oxazoles

By Qi Zhang Jin,* Guy J. Hartman and Chi-Tang Ho, Department of Food Science, Cook College, New Jersey Agricultural Experiment Station, Rutgers, The State University of New Jersey, New Brunswick, New Jersey

Oxazoles and oxazolines are a class of compounds which have been found in heated foodstuffs at low concentrations. They are characterized by possessing a five-membered ring with oxygen and nitrogen in the 1 and 3 positions. Their strong odor impact at low concentration suggests they may be important contributors to food aroma.

The occurrence of oxazoles in food flavor has been reviewed.¹⁻³ More recently, oxazoles have been identified in baked potato,⁴ roasted peanuts,^{5,6} roasted beef,⁷ cocoa butter⁸ and fried chicken.⁹ Oxazoles have also been reported in various model systems, namely, furfural, hydrogen sulfide and ammonia,¹⁰ rhamnose and ammonia,¹¹ D-glucose and ammonia,¹² maltol and ammonia¹³ and diacetyl and alkyl-^{14,15} or sulfur-containing amino acids.^{16,17}

The aroma properties of fifteen 4,5-dialkyloxazoles have been reported.¹⁸ Most of the 4,5-dialkyloxazoles synthesized have green, vegetable-like aromas. It was also noted that 4-butyl-5-propyloxazole, 4-butyl-5-methyloxazole and 4-pentyl-5-methyloxazole were judged to have a strong bell pepper-like character. This observation indicates that the general structure for compounds possessing potent bell-pepper aroma



where R is a hydrocarbon chain about four carbons long and X is oxygen or sulfur, which was proposed by Buttery et al.¹⁹ could be extended to 4,5-dialkyloxazoles.

*Present address: Scientific Research Institute of Fragrance and Flavor Industry, Ministry of Light Industry, Shanghai, People's Republic of China.

Aroma properties for some alkyloxazoles and oxazolines have also been summarized by other reviewers.¹⁻³ Oxazoles and 3-oxazolines were reported to have aromas ranging from nutty and cocoa to green vegetable-like characteristics while 2-oxazolines were described as fruit-like. 2-Oxazolines are not commonly reported as naturally occurring.

Recently we reported the synthesis and mass spectral properties of fifty alkyloxazoles.²⁰ In this paper, the aroma properties of those alkyloxazoles are reported. In addition, the aroma properties of two sulfur-containing oxazoles are reported which were identified in a methionine-diacetyl model system and subsequently synthesized.¹⁵

Experimental

Materials. Aliphatic ketones, aliphatic aldehydes, bromine, amides, and acids were obtained from Aldrich Chemical Co.

Synthesis of α -Bromo Ketones. These were synthesized by the methods described by Catch et al.,²¹ which involves essentially direct bromination of the appropriate ketone. With unsymmetrical ketones, two bromoketones are formed. In all cases, the mixture of the two bromides was taken through the oxazole synthesis and the two isomeric oxazoles were separated by GC.

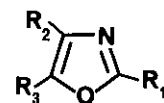
Synthesis of α -Bromo Aldehydes. These were synthesized by the method of Bedoukian,²² which involves conversion of the corresponding saturated aldehyde to its enol acetate followed by the addition of bromine and then conversion to the dimethyl acetal and hydrolysis to the α -bromo aldehyde.

Synthesis of Alkyloxazoles. These were all synthesized by the method of Theilig.²³ One

Table I. Aroma Qualities of Synthetic Alkylloxazoles

<u>Alkylloxazole</u>	<u>Occurence in Food</u>	<u>Aroma Description</u>
5-butyloxazole	fried bacon (24)	fatty, animalic, bacon-fatty
2-methyl-5-propyloxazole		sweet, fruity, fatty, slightly nutty
2,4-diethyloxazole		acidic, smoky
5-pentyloxazole		fatty, green, animalic fatty, bacon-fatty
2,4-dimethyl-5-propyloxazole		green, vegetable-like
2-methyl-4,5-diethyloxazole		sweet, earthy
2-methyl-4-butyloxazole		green, floral
2,4-diethyl-5-methyloxazole		strong green, flowery
2-propyl-4-ethyloxazole		acidic, cheesy, fruity, fatty
2-butyl-4-methyloxazole		very sweet, spicy, nutmeg, butter-like
2-methyl-5-pentyloxazole		sweet, strong floral, fatty waxy
2,4-dimethyl-5-butyloxazole		dry herb-like, seasoning herb-like
2-methyl-4-ethyl-5-propyloxazole	cocoa butter (8) french fried potato (25)	green, fatty, vegetable-like
2,5-dimethyl-4-butyloxazole	cocoa butter (8) roasted beef (7)	fresh acidic green note, pickle-like
2-methyl-4-propyl-5-ethyloxazole		green, flowery, sweet, earthy
2-ethyl-5-butyloxazole		green, fatty, sweet, slightly cooling effect
2-propyl-4-methyl-5-ethyloxazole		very sweet, fruity
2-propyl-4-ethyl-5-methyloxazole		sweet acidic, slightly cheese, slightly fruity
2,4-dipropyloxazole		acidic, green, spicy, cheesy
2-butyl-4,5-dimethyloxazole	french fried potato (25)	sour, buttery, cheese cake-like
2-pentyl-4-methyloxazole		very sweet, herbal
2,4-dimethyl-5-pentyloxazole		sweet, floral, fruity, slightly green
2-methyl-4-ethyl-5-butyloxazole	cocoa butter (8)	acidic, fatty, sweet, flowery, afternote
2,5-diethyl-4-propyloxazole		sweet, floral, slightly green-fatty
2-ethyl-4-butyl-5-methyloxazole		fatty, sweaty
2-butyl-4-ethyl-5-methyloxazole	cocoa butter (8)	green, slightly buttery, weak acid
2-pentyl-4,5-dimethyloxazole	french fried potato (25)	fennel-like, earthy, green
2-hexyl-4-methyloxazole		very sweet, floral, herbal
2,4-diethyl-5-butyloxazole		green, fruity, brown
2-ethyl-4-pentyl-5-methyloxazole		mushroom-fatty note, sweet
2-butyl-4-methyl-5-propyloxazole		green, sweet, green pepper-like
2-butyl-4,5-diethyloxazole	french fried potato (25)	tropical fruit-like, acidic
2-butyl-4-propyl-5-methyloxazole	french fried potato (25)	fatty, rubbery
2-pentyl-4-methyl-5-ethyloxazole		buttery, sweet, lactone-like
2-pentyl-4-propyloxazole		sweet, slightly herbal, acidic
2-hexyl-4,5-dimethyloxazole	french fried potato (25)	very fresh flowery
2-hexyl-4-ethyloxazole		fatty, sweet, slightly floral
2-heptyl-4-methyloxazole		sweet, floral
2,5-dibutyl-4-methyloxazole	cocoa butter (8)	green, slightly floral
2-pentyl-4-methyl-5-propyloxazole		green, nutty
2-pentyl-4-butyloxazole		cocoa, sweet, nutty
2-hexyl-4-ethyl-5-methyloxazole		very fatty, sweet, french fried potato-like
2-hexyl-4-propyloxazole		very fatty, deep-fat fried, little green
2-heptyl-4,5-dimethyloxazole		sweet, herbal, flowery
2-heptyl-4-ethyloxazole		weak herbal
2-octyl-4-methyloxazole		waxy, shortening-like, slightly sweet
2-(2-methylthioethyl)-4,5-dimethyl-3-oxazoline		french fried potato-like, fatty chicken-like
2-(2-methylthioethyl)-4,5-dimethyl-oxazole		overcooked cabbage

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equivalent of α -bromo or α -bromo aldehyde was allowed to react with two equivalents of amide. Yields were all generally quite satisfactory at about 50%. 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 alkyloxazoles were subjected to aroma evaluation.

Results and Discussion

The aroma qualities of the alkyloxazoles synthesized were described by a panel of three experienced flavorists and are listed in Table I. Most of the alkyloxazoles have green, sweet aromas.

It is interesting to note that 5-butyloxazole and 5-pentyloxazole had a very distinct bacon-fatty aroma. 5-Butyloxazole was identified in the volatile flavor constituents of fried bacon²⁴ and could be important to fried bacon aroma. Both 5-butyloxazole and 5-pentyloxazole have hydrocarbon chains about four carbons long substituted at the carbon-5 of the oxazole ring and no alkyl group on carbon-2 or carbon-4 of the oxazole ring. When a methyl or ethyl group is substituted at the carbon-2 position, as in the case of 2-methyl-5-butyloxazole, 2-methyl-5-pentyloxazole and 2-ethyl-5-butyloxazole, the strength of fatty aroma is reduced and sweet and floral aromas become more characteristic. When both the carbon-2 and carbon-4 are substituted by a methyl or ethyl group like 2,4-dimethyl-5-pentyloxazole and 2-methyl-4-ethyloxazole, the aroma is also dominated by sweet and floral characteristics.

Other oxazoles identified in foods and whose sensory properties are reported here are less characteristic of the food in which they were

identified. Some of these oxazoles possess fatty characteristics but are less specific than the 5-alkyloxazoles in the type of fatty food (i.e., cocoa butter, french fries).

The aroma characteristics of these oxazoles suggest that they may be more important to the background of heated foodstuffs rather than "character" impact compounds. They may be of greater use in fresh foods or perfume application.²

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