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REVIEW

Pyrroles in Foods

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This review covers the occurrence of pyrrole derivatives in food systems as well as their formation in model systems and organoleptic properties.

Pyrroles represent a minor class of potentially significant flavor-associated compounds that were found to be naturally occurring in foods in the mid-1960s. Since then it has been determined that they are primarily formed thermally with other formation pathways existing. Because they possess unique organoleptic properties, certain pyrroles are utilized as flavor additives. Thus, in this review an attempt will be made to summarize their food occurrences, sensory properties, and formation in model systems.

FOOD OCCURRENCES

To date ~20 pyrrole derivatives have been identified as occurring in food systems. Thus, compared to other heterocyclic compounds, such as pyrazines, this represents a relatively small number. They were first identified in the mid-1960s in coffee (Merritt et al., 1963; Viani et al., 1965; Gianturco et al., 1966) and are still currently being reported in foods. It can be seen from Table I that the foods in which they have been identified are rather limited. It is also interesting to note that all the food systems listed in Table I have undergone some degree of either thermal treatment or microbial activity. Thus, it does not appear that pyrroles are present in fresh, raw foods.

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ORGANOLEPTIC PROPERTIES

The fact that certain pyrrole derivatives have unique and potent organoleptic properties can be appreciated by viewing the data in Table II. These six pyrroles are on the Food and Drug Administration GRAS (Generally Recognized As Safe) list. Data compiled by FEMA (Flavor and Extract Manufacturer's Association) indicate that all are used in the low ppm range in flavoring formulations.

The actual aromas and flavors associated with pyrroles perhaps can be best described by viewing the data summarized in Table III. This listing represents the descriptions resulting from the addition of low ppm levels of the various synthesized compounds to either a sugar solution or instant coffee, and as can be seen, this resulted in both desirable and undesirable characteristic sensations.

Interestingly, other than that reported in patents, few researchers have extensively investigated the organoleptic properties of pyrroles, including the evaluation of their threshold values. However, several brief mentions of their sensory properties have appeared. For example, Watanabe and Sato (1972) reported that 2-acetylpyrrole added a slightly caramel-like character to the flavor of cooked beef. Also in beef, Peterson et al. (1975) described the odors of 2-acetylpyrrole and 2-formylpyrrole, both of which they identified in canned beef stew as being unpleasant and reminiscent of heated plastic or antiseptic-like. They in turn concluded that these odors could contribute to overall undesirable retort flavor associated with canned beef. In

Table I. Food and Related Systems in Which Pyrroles Have Been Identified

system	reference
almonds (roasted)	Takei et al. (1974); Takei and Yamanishi (1974)
asparagus (cooked)	Tressl et al. (1977)
barley (roasted)	Harding et al. (1978)
beef (boiled, roasted, fried, canned)	Liebich et al. (1972); Watanabe and Sato (1972); Peterson et al. (1975); Coppock and MacLeod (1977); MacLeod and Coppock (1976, 1977)
beer	Harding et al. (1977)
cake	Takei (1977)
casein	Ferretti et al. (1970); Ferretti and Flanagan (1971a); Kato et al. (1972a)
chocolate	Marion et al. (1967); van der Wal et al. (1968, 1971); Maniere and Dimick (1979)
coffee	Merritt et al. (1963); Viani et al. (1965); Gianturco et al. (1966); Heins et al. (1966); Raymond et al. (1966); Bondarovich et al. (1967); Stoll et al. (1967); Stoffelsma and Pypker (1968); Stoffelsma et al. (1968); Vitzthum and Werkhoff (1976)
corn silk	Flath et al. (1978)
eggs (heated)	MacLeod and Cave (1975, 1976)
filberts (roasted)	Kinlin et al. (1972); Sheldon et al. (1972)
licorice	Frattini et al. (1977)
malt extract	Farley and Nursten (1980)
mushroom (dried)	Thomas (1973)
orange powder	Tatum et al. (1967)
peanuts (roasted)	Johnson et al. (1971); Walradt et al. (1971)
popcorn	Walradt et al. (1970)
pork liver (cooked)	Mussinan and Walradt (1974)
potato chips	Buttery and Ling (1972)
soy sauce	Nunomura et al. (1976, 1978)
rice (wild)	Withycombe et al. (1978)
tea (roasted)	Yamanishi et al. (1973)
tobacco	Demole and Berthet (1972); Roeraade and Enzell (1972)
whey	Ferretti and Flanagan (1971b,c)

Table II. FEMA-Utilized Pyrroles^a

compound	FEMA no.	av usage level, ppm
1-ethyl-2-acetylpyrrole	3147	5
1-methyl-2-acetylpyrrole	3184	10
2-acetylpyrrole	3202	50
<i>N</i> -furfurylpyrrole	3284	2
pyrrole	3386	3
2-propionylpyrrole	3614	0.15

^a From Hall and Oser (1970), Oser and Ford (1979), and Furia and Bellanca (1975).

working with popcorn, Walradt et al. (1970) mentioned that *N*-furfurylpyrrole had a green haylike aroma and as such could contribute to the aroma and flavor of this food item. Shigematsu et al. (1972) made some general comments relative to the odor properties of pyrrole derivatives. They stated that alkyl- and acylpyrroles had unfavorable odors but that dilute concentrations of alkylpyrroles had a sweet, slightly burntlike aroma. Shigematsu et al. (1977) have reported that both 2-acetyl-1-isobutylpyrrole and 1-isobutyl-5-methylpyrrole-2-aldehyde have a characteristic sweet, slightly minty, cinnamon-like odor.

Table III. Organoleptic Properties of Various Synthesized Pyrroles^a

compound	property
1-ethylpyrrole	burnt
1-(<i>n</i> -amyl)pyrrole	green, fatty
1-isoamylpyrrole	fatty, aldehyde-like
1-(α -methylbutyl)pyrrole	green
1-(5-methyl-2-furfuryl)pyrrole	fruity, earthy, mushroomlike
1-thienylpyrrole	gooseberry, geranium, green, rubbery
1-ethylpyrrole-2-aldehyde	burnt, roasted
1-butylpyrrole-2-aldehyde	mint
1-butylpyrrole-3-aldehyde	bready
1-amylpyrrole-2-aldehyde	honeylike
1-amylpyrrole-3-aldehyde	fatty, green, caraway-like
1-(α -methylbutyl)pyrrole-2-aldehyde	slightly minty
1-(α -methylbutyl)pyrrole-3-aldehyde	earthy
1-furfurylpyrrole-2-aldehyde	burnt, acid
1-furfurylpyrrole-3-aldehyde	astringent, bitter, cereal-like
1-thienylpyrrole-2-aldehyde	earthy, caramel
1-isoamylpyrrole-2-aldehyde	fatty, flowery
1-furfuryl-2-acetylpyrrole	fruity, roselike
1-thienyl-2-acetylpyrrole	green
1-thienyl-3-acetylpyrrole	green, geranium
1-acetylpyrrole	astringent, bitter, roasted
1-propionylpyrrole	astringent, peanut, roasted
2-methyl-5-acetylpyrrole	bitter, earthy, roasted
1,2-dimethyl-5-acetylpyrrole	grapelike, fatty, bitter, roasted
2,5-dimethyl-3-acetylpyrrole	weak, sweet
1-methyl-3-acetylpyrrole	woody
pyrrol-2-ylpropane-1,2-dione	bitter, roasted, peanut
pyrrol-2-ylbutane-1,2-dione	buttery, meaty
<i>N</i> -methylpyrrol-2-yl methyl sulfide	metallic, burnt
<i>N</i> -methylpyrrol-2-yl ethyl sulfide	metallic, earthy, burnt
<i>N</i> -methylpyrrol-2-yl furfuryl sulfide	astringent, sulfurous, green
(<i>N</i> -methylpyrrol-2-yl)methylthiol acetate	metallic, sulfurous, burnt

^a From Winter et al. (1972, 1975, 1976a,b).

MODEL SYSTEM STUDIES

As reviewed by Hodge et al. (1972), nonenzymatic browning reactions can lead to the formation of numerous flavor-producing compounds, including pyrroles. This has been verified by numerous researchers in working with model browning systems. At this point a chronological summary relative to pyrrole identification in model systems will be given.

Kobayasi and Fujimaki (1965) identified pyrrole and *N*-acetylpyrrole among the resulting compounds when hydroxyproline and glucose were heated under nitrogen at temperatures ranging from 120 to 200 °C. Langner and Tobias (1967) heated either glucose or lactose with glycine, lysine, valine, or casein. 2-Acetylpyrrole was identified among the 38 gas chromatographic peaks observed, and it was found that independent of nitrogen source, glucose produced more of the compound than lactose.

Kato and his group have investigated pyrrole derivative formation due to browning reactions rather extensively. For example, Kato (1966) found that heating *D*-xylose with *n*-butylamine formed *N*-(*n*-butyl)pyrrole-2-carboxaldehyde whereas when methylamine was utilized, *N*-methylpyrrole-2-carboxaldehyde resulted. Later, Kato (1967) postulated that the reaction proceeded through the intermediate 3-deoxy-*D*-pentose. Kato and Fujimaki (1968)

reported on the formation of a series of N-substituted pyrrole-2-carboxaldehydes when D-xylose was thermally reacted with various amino acids including glycine, alanine, and leucine. They also reported N-substituted pyrrole-2-carboxaldehydes were stable to further heating and thus would not be readily available as intermediates for the formation of other flavor-related compounds. This could possibly be an explanation as to why relatively few pyrroles have been found. The pyrolysis of threonine has been shown to result in the formation of pyrrole, 2-methylpyrrole, and 3-methyl-4-ethylpyrrole by Kato et al. (1970). Upon the reaction of D-glucose with butyl-, ethyl-, or methylamine, Kato and Fujimaki (1970) identified a series of N-substituted 5-(hydroxymethyl)pyrrole-2-aldehydes which were described as having no odor in the pure state but formed a roasted flavor upon decomposition due to their relative instability upon further heating. A later study by Shigematsu et al. (1971) involving the roasting at temperatures in the area of 200–250 °C of D-glucose with several alkyl- α -amino acids resulted in the identification of a series of 2-[5-(hydroxymethyl)-2-formylpyrrol-1-yl]-alkyl acid lactones. Specific pyrrole lactones identified included propionic acid lactone, *n*-butyric acid lactone, isovaleric acid lactone, and isocaproic acid lactone. Further work by Shigematsu et al. (1972) resulted in the isolation and identification of 16 alkyl- and acylpyrroles, alkylpyrrole-2-aldehydes, and furfurylpyrroles from a mixture of DL- α -alanine and D-glucose that had been heated for 1 h at 250 °C. The major pyrrole derivatives found in this study included 1-ethylpyrrole, 1-ethyl-5-methylpyrrole-2-aldehyde, and 2-acetylpyrrole. The heating of L-rhamnose and ethylamine at 100 °C for 1 h has also been shown to result in the formation of pyrroles (Kato et al., 1972b). A series of pyrrole lactones, pyrrole-2-aldehydes, and 2-acetylpyrroles were identified by Shigematsu et al. (1977) when several Amadori compounds were pyrolyzed at 200 °C for varying periods of time. Recently, Nakayama et al. (1980) observed the formation of ϵ -[2-formyl-5-(hydroxymethyl)pyrrol-1-yl]-L-norleucine during the thermal reaction of L-lysine and D-glucose. The lysine-lactose browning system investigated by Ferretti and Flanagan (1973) also showed the presence of pyrroles, namely, 2-acetylpyrrole.

High-temperature (840 °C) pyrolysis of various compounds also has been shown to result in pyrrole derivative formation. In the case of proline, Higman et al. (1970) found pyrrole to be the major decomposition product along with indole and postulated that pyrrole represented an intermediate in the formation of indole from proline. In addition, large amounts of pyrrole were found when casein and collagen were pyrolyzed.

Four pyrrole derivatives were among the 13 compounds identified when D-glucose was thermally reacted under acidic conditions with methylamine (Jurch and Tatum, 1970). Among the compounds reported for the first time in this study were 2-(2-hydroxyacetyl)-1-methylpyrrole and 5-(hydroxymethyl)-1-methylpyrrole-2-carboxaldehyde. Four pyrroles were also among the 45 compounds identified by Mulders (1973) when he thermally reacted cysteine-cystine with ribose. The work of Rizzi (1974) clearly demonstrated that pyrroles can also be formed by the thermal reaction of furan derivatives with α -amino acids. Glyoxal, glycine, and lactose-casein model systems were shown by Velisek et al. (1976) to contain 2-pyrrole-aldehyde.

The work of Olsson et al. (1977, 1978) and Olsson and Pernemalm (1979) has greatly expanded on the identification of aromatic compounds resulting from the thermal

reaction of D-glucose with other reactive compounds under acidic conditions. In the case of glucose-methylamine, a total of 19 compounds were identified, including 6 pyrrole derivatives (Olsson et al., 1977). With glucose-glycine as the reactants, 8 of the 28 compounds identified were pyrroles. Olsson and Pernemalm (1979) outlined method of synthesis of the pyrroles they had previously identified. Shaw and Berry (1977) investigated volatile compounds formed during the thermal treatment of several model systems including fructose-alanine, fructose- γ -aminobutyric acid, and rhamnose-alanine. No pyrroles were observed in the latter system while in the second model only 2-acetylpyrrole was identified and both 2-acetylpyrrole and 5-methylpyrrole-2-carboxaldehyde appeared in the first. They attempted to discuss these differences relative to possible formation mechanisms and concluded that more than one pathway for their formation is suggested.

Shibamoto and co-workers have recently extensively reported on the formation of numerous volatiles from model systems. For example, Shibamoto and Russell (1977) identified 51 compounds resulting from a D-glucose-hydrogen sulfide-ammonia-water system. Interestingly, the only pyrrole derivative identified in this study was pyrrole itself. Likewise, only 2 pyrrole derivatives were among the 17 identified by Shibamoto (1977) when furfural, hydrogen sulfide, and ammonia were reacted. However, Shibamoto and Bernhard (1978) identified 13 pyrrole derivatives when they thermally reacted L-rhamnose with ammonia, with pyrrole representing 3.75 wt % of the total compounds identified. In their last study (Shibamoto et al., 1979) involving the reaction of D-glucose with ammonia, nine pyrroles were identified. In this study, they concluded that a high degree of sugar fragmentation is required to form pyrroles. This is a possible explanation as to why there are apparent discrepancies in the literature as to the number and types of pyrroles that have been isolated and identified in various model systems.

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