

Pyrazines in Foods. A Review

Joseph A. Maga* and Charles E. Sizer

Numerous pyrazine compounds have been reportedly isolated from various food systems. Other studies have demonstrated the importance of these compounds in the flavor of heated and toasted foods. Relatively harsh methods have

been reported for their isolation. This review lists the pyrazines and outlines the various theories and practices surrounding pyrazine formation and their isolation from foods.

The flavor of foods has always been an interesting and complicated area worthy of investigation. Through the years many classes of compounds have been implicated as the key to the flavor properties of certain foods. During the past decade, evidence has been accumulating that a class of heterocyclic nitrogen-containing compounds, namely pyrazines, directly contributes to the roasted or cooked flavor of foods.

The purposes of this review are: to compile a list of the pyrazine compounds found to date in various food systems; to discuss the flavor properties of pyrazines; to discuss the current theories associated with the formation of these compounds; and to outline the various methods reported for the isolation of pyrazine compounds important in food flavor.

OCCURRENCES IN FOODS

Food systems that have been found to contain pyrazine compounds include beef products (Liebich *et al.*, 1972; Watanabe and Sato, 1971a,b), toasted barley (Collins, 1971; Wang *et al.*, 1969), cocoa products (Dietrich *et al.*, 1964; Flament *et al.*, 1967; Marion *et al.*, 1967; Rizzi, 1967; van Praag *et al.*, 1968, van der Wal *et al.*, 1968, 1971), coffee (Bondarovich *et al.*, 1967; Goldman *et al.*, 1967; Reichstein and Staudinger, 1928; Raymond *et al.*, 1966; Stoffelsma *et al.*, 1968; Viani *et al.*, 1965), peanuts (Johnson *et al.*, 1971; Mason *et al.*, 1966; Walradt *et al.*, 1971), popcorn (Walradt *et al.*, 1970), potato products (Buttery *et al.*, 1970, 1971; Deck and Chang, 1965; Sapers *et al.*, 1971), rye crisp bread (von Sydow and Anjou, 1969), soy products (Kosuge *et al.*, 1962; Manley and Fager-son, 1970; Wilkens and Lin, 1970), tomatoes (Ryder, 1966), peas (Murray *et al.*, 1970), green bell peppers (Buttery *et al.*, 1969a,b), sesame oil (Takei *et al.*, 1969), dairy products (Ferretti and Flanagan, 1971a,b, 1972; Ferretti *et al.*, 1970), roasted pecans (Wang and Odell, 1972), roasted filberts (Sheldon *et al.*, 1972) and chicken broth (Wilson and Katz, 1972).

A detailed list of pyrazine compounds identified from the above foods can be found in Table I. Interestingly, most of these compounds have been found in foods that are typically toasted or roasted in their preparation or involve an extended heat treatment in their isolation procedure. Several exceptions would be the isolation of several methoxypyrazines from bell peppers (Buttery *et al.*, 1969a,b), the identification of 2,5-dimethylpyrazine in potato chips (Deck and Chang, 1965), and in the identification of volatile flavor compounds from roasted filberts (Sheldon *et al.*, 1972). In these latter studies extraction and isolation were performed using relatively mild procedures.

FLAVOR PROPERTIES

Although most investigators agree that pyrazine compounds contribute significantly to the flavor of certain foods, few have actually reported on the flavor and odor

properties of individual compounds or their concentration as found in foods.

A specific pyrazine compound that has been associated with potato flavor is 2,5-dimethylpyrazine (Deck and Chang, 1965). The authors isolated this compound from potato chips and determined its flavor threshold to be 2 ppm in oil and 1 ppm in water. At a concentration of 10 ppm in oil the authors report this compound to have an earthy, raw potato flavor. Buttery *et al.* (1970) briefly mentioned that in their opinion 2-methoxy-3-ethylpyrazine also has an odor similar to raw potatoes. In a later study, Buttery *et al.* (1971) concluded that because of its low threshold, 2-ethyl-3,6-dimethylpyrazine could be considered important to potato chip aroma.

The use of synthesized methoxypyrazines to enhance the flavor of various potato products has been reported (Guadagni *et al.*, 1971). They concluded that 2-methoxy-3-ethylpyrazine, at levels of 0.1-0.2 ppm, was capable of increasing the potato flavor level of dehydrated potatoes, potato salad, dehydrated scalloped potatoes, and potato soup.

A methoxypyrazine (2-methoxy-3-isobutylpyrazine) has been reported to produce the characteristic odor of green bell peppers (Buttery *et al.*, 1969b). This compound was found to have an odor threshold of 0.002 ppb in water. In another study (Buttery *et al.*, 1969b) the authors again reaffirmed the importance of 2-methoxy-3-isobutylpyrazine in bell pepper odor characterization and stated that approximately 75% of an untrained panel characterized the odor of this compound at levels of from 100 to 300 ppb in water as being similar to that of green bell peppers.

Seifert *et al.* (1970, 1972) reported the threshold and flavor properties of various synthesized methoxypyrazines. The results of these studies are summarized in Table II. Thus, these data demonstrate that pyrazine compounds can be synthesized that possess characteristic odors of low thresholds. However, Seifert *et al.* (1970) noted that synthesized pyrazinones and hydroxyalkylpyrazines were relatively odorless. The odor potency of methoxypyrazines was also verified by Murray *et al.* (1970), who isolated 2-methoxy-3-isopropyl-, 2-methoxy-3-*s*-butyl-, and 2-methoxy-3-isobutylpyrazine from green peas.

The probable flavor contribution of pyrazine compounds from roasted barley on beer flavor was investigated by Collins (1971). A summary of this work is shown in Table III. Thus, in a beer system, the dimethylethylpyrazines were found to have extremely low flavor thresholds.

Two reports indicate that the flavor properties of 2-acetylpyrazine closely resemble popcorn. The first report appeared as a patent (Roberts, 1968) and it claims that from 0.00005 to 0.3% by weight of 2-acetylpyrazine incorporated into food will impart a popcorn-like flavor and aroma. This was later confirmed by the work of Walradt *et al.* (1970).

Kosuge and Kamiya (1962) reported that tetramethylpyrazine, which they isolated as a by-product of *Bacillus subtilis* growth, had a characteristic fermented soybean smell.

Recently Koehler *et al.* (1971) reported on the odor

*Department of Food Science and Nutrition, Colorado State University, Fort Collins, Colorado 80521.

thresholds of various pyrazines. These data are summarized in Table IV. As can be seen, there was a wide range in odor thresholds among the pyrazines evaluated. In this same study an attempt was made to quantitate several pyrazines isolated from foods and to postulate on their possible flavor contribution in light of their determined threshold values. The three pyrazines specifically quantitated in coffee, roasted peanuts, and potato chips were pyrazine, 2-methylpyrazine, and dimethylpyrazine. Based upon their isolation and quantitation techniques, the authors concluded that pyrazines can contribute significantly to the flavor of coffee and roasted peanuts but not in potato chips due to the small amount of pyrazines isolated from the latter.

The possible flavor importance of synthesized pyrazine derivatives is exemplified by the recent publication of Mookherjee and Klaiber (1972). They reported on a relatively simple procedure for converting alkylpyrazines into their corresponding acetylpyrazines. Thus, they were able to form 3-methyl- and 3-ethyl-2-pyrazinyl methyl ketone. However, the authors did not report on the flavor properties of these compounds.

The relative flavor importance of pyrazine compounds can also be evaluated in light of the recent number of patents issued in the area. Typical examples include chocolate flavors (Nakel and Hiler, 1971; van Praag and Bidmead, 1971), nut-like flavor (Winter, 1971), coffee flavor (Polak's Frutal Works, 1972) and "baked" flavor (Firmenich *et al.*, 1967). Other patents which propose the use of acetylpyrazines as flavoring materials include those of Roberts (1968), Winter *et al.* (1968), and Smith *et al.* (1954).

The quantitation of pyrazines in foods has been greatly neglected. Most attempts at quantitation have taken the form of reporting relative amounts such as small, medium, and large concentrations (Wang and Odell, 1972).

Recently Reineccius *et al.* (1972) attempted to use glc and internal standards as a means of quantitating the specific pyrazine content of roasted cocoa beans. They reported that losses of internal pyrazine standards may run as high as 30% due to the procedures employed. Thus, a real need exists for a reliable quantitation method.

PYRAZINE FORMATION THEORIES

The role of carbohydrate degradation on pyrazine formation is well documented (Hodge, 1953; Hodge *et al.*, 1972) and early reports exist of the isolation of substituted pyrazines from reaction mixtures of ammonia and hexose sugars (Brandes and Strohr, 1896; Davison and Wiggins, 1956; Hough *et al.*, 1952; Irvine *et al.*, 1913; Wiggins and Wise, 1955).

Theories exist for the formation of various types of pyrazines. In the case of simple alkylated pyrazines, Dawes and Edwards (1966), using model systems containing fructose and amino acids, identified 2,5-dimethyl- and trimethylpyrazine and concluded that pyrazines in heated foods resulted from the condensation reactions between sugars and amino acids. At approximately the same time, Mason *et al.* (1966) followed changes which occurred in sugar and amino acid contents during peanut roasting and also concluded that pyrazines resulted from the reaction intermediates of amino acids and sugars.

Newell *et al.* (1967), as a result of their work with peanuts, proposed a pyrazine formation mechanism involving amino acids and sugars. Essentially it involved the addition of an amino acid to the anomeric portion of the carbohydrate, followed by dehydration to yield an enaminol which in turn became the Schiff base cation through the loss of an hydroxy ion. In turn, the base cation became an imine through decarboxylation and then the imine could hydrolyze to an aldehyde and a dieneamine. Enolization

of the dieneamine yielded the unsaturated ketoamine which, in turn, condensed to yield amino acetone and glyceraldehyde. Two molecules of amino acetone then condensed to yield 2,5-dimethylpyrazine.

The possible role of ammonia in pyrazine formation was reported by van Praag *et al.* (1968). They reacted fructose with a variety of amino acids and found a similar series of pyrazines formed in all cases. Thus, they concluded that ammonia was the intermediate.

Koehler *et al.* (1969) used radioisotopic labeling techniques in an effort to establish the source materials for pyrazine formation. They concluded that the carbon in pyrazine compounds came from the sugar and that nitrogen from amino acids contributed the nitrogen portion. Thus, they disproved the theory that ammonia or the ammonium ion itself was the major nitrogen source, since it was found that when ammonium salts were reacted, different pyrazine formation patterns than amino acid reaction patterns occurred. Also, they demonstrated that different amino acids gave different pyrazine yields.

The probable method of carbon incorporation from carbohydrates was also investigated (Koehler *et al.*, 1969). These results indicated that glucose fragments incorporated into pyrazines had split predominantly between carbons 2 and 3 from the anomeric end of the molecule, thus indicating that the 6-carbon intermediate leading to this split was dissymmetrical. However, when the split occurred between carbons 3 and 4, the two resulting 3-carbon fragments are equivalent and thus the 6-carbon intermediate was symmetrical.

In a later publication, Koehler and Odell (1970) reported on the variables that can affect pyrazine formation in a sugar-amino acid model system. Reaction temperatures of from 80 to 150° demonstrated that few, if any, pyrazines were formed at temperatures of less than 100°, but pyrazine yield began at 100° and increased as temperature increased. Yield became variable above 150° and the authors postulated that this was due to pyrazine destruction after their formation. Using 120° conditions and varying reaction times, it was found that pyrazine formation increased rapidly for up to 24 hr and then leveled off with only a gradual increase at the end of 72 hr.

In a similar study (Reineccius *et al.*, 1972) which used an actual food system (cocoa beans) instead of a model system, pyrazine formation was found to be quite rapid and linear during the first 30 min of roasting at 150°. This later study (Reineccius *et al.*, 1972) also demonstrated that, in the case of cocoa beans, pyrazine formation can occur at time-temperature relationships as low as 30 min at 70°. Apparently, the ratio of sugar to amino acid can also affect pyrazine formation, since ratios other than 1:1 generally decreased pyrazine yield when measured in a model system (Koehler and Odell, 1970).

Even though sugars and amino acids are thought to be the major precursors of pyrazines, the actual amounts of these products utilized during the roasting of cocoa beans have been reported to represent only approximately 0.2% of the sugars and amino acids available (Reineccius *et al.*, 1972). As would be expected, acidic conditions lowered yield, whereas basic conditions increased yield as the result of increased reactivity of the amino group and to the greater degree of rearrangement and fragmentation of sugars under basic conditions (Koehler and Odell, 1970). This study also verified their previous study (Koehler *et al.*, 1969) in that certain amino acids yielded more pyrazine material than other amino acids. Carbon source (glucose, fructose, sucrose, arabinose) also was found to affect yield when reacted with asparagine. The fructose carbon source yielded more pyrazines, probably due to the greater ability of fructose to fragment.

Koehler and Odell (1970) also demonstrated that be-

Table I. Reported Pyrazine Compounds in Foods

Pyrazine	Food	Reference
Unsubstituted	Barley (roasted)	Collins (1971)
	Casein	Ferretti <i>et al.</i> (1970)
	Coffee	Viani <i>et al.</i> (1965)
		Reymond <i>et al.</i> (1966)
		Bondarovich <i>et al.</i> (1967)
		Goldman <i>et al.</i> (1967)
		Stoffelsma <i>et al.</i> (1968)
		Walradt <i>et al.</i> (1971)
		Walradt <i>et al.</i> (1970)
		von Sydow and Anjou (1969)
		Wilkens and Lin (1970)
		Manley and Fagerson (1970)
		Wang <i>et al.</i> (1969)
		Collins (1971)
2-Methyl-	Beef (shallow fried)	Watanabe and Sato (1971b)
	Casein	Ferretti <i>et al.</i> (1970)
	Chicken broth	Wilson and Katz (1972) (T) ^a
	Cocoa products	Rizzi (1967)
		van Pragg <i>et al.</i> (1968)
		Reineccius <i>et al.</i> (1972)
	Coffee	Viani <i>et al.</i> (1965)
		Reymond <i>et al.</i> (1966)
		Bondarovich <i>et al.</i> (1967)
		Goldman <i>et al.</i> (1967)
		Stoffelsma <i>et al.</i> (1968)
		Sheldon <i>et al.</i> (1972)
		Ferretti and Flanagan (1972)
		Mason <i>et al.</i> (1966)
	Johnson <i>et al.</i> (1971)	
	Walradt <i>et al.</i> (1971)	
	Wang and Odell (1972)	
	Walradt <i>et al.</i> (1970)	
	Sapers <i>et al.</i> (1971)	
	Buttery <i>et al.</i> (1971)	
	von Sydow and Anjou (1969)	
	Wilkens and Lin (1970)	
	Manley and Fagerson (1970)	
	Ryder (1966)	
	Ferretti and Flanagan (1971a)	
2,3-Dimethyl-	Barley (roasted)	Collins (1971)
	Beef (boiled)	Liebich <i>et al.</i> (1972) (NESR)
	Beef drippings (roasted)	Liebich <i>et al.</i> (1972) (T) (NESR)
	Beef (shallow fried)	Watanabe and Sato (1971b)
	Casein	Ferretti <i>et al.</i> (1970)
	Cocoa products	Flament <i>et al.</i> (1967); Rizzi (1967)
		van Praag <i>et al.</i> (1968)
		Reineccius <i>et al.</i> (1972)
	Coffee	Reymond <i>et al.</i> (1966)
		Bondarovich <i>et al.</i> (1967)
		Stoffelsma <i>et al.</i> (1968)
		Sheldon <i>et al.</i> (1972)
		Ferretti and Flanagan (1972)
		Johnson <i>et al.</i> (1971)
	Walradt <i>et al.</i> (1971)	
	Wang and Odell (1972)	
	Walradt <i>et al.</i> (1970)	
	Buttery <i>et al.</i> (1971)	
	von Sydow and Anjou (1969)	
	Wilkens and Lin (1970)	
	Manley and Fagerson (1970)	
	Ferretti and Flanagan (1971a)	
2,5-Dimethyl-	Barley (roasted)	Wang <i>et al.</i> (1969)
		Collins (1971)
	Beef (shallow fried)	Watanabe and Sato (1971b)
	Beef fat (heated)	Watanabe and Sato (1971a)
	Casein	Ferretti <i>et al.</i> (1970)
	Cocoa products	Flament <i>et al.</i> (1967)
		van Praag <i>et al.</i> (1968)

Table I (Continued)

Pyrazine	Food	Reference	
2,6-Dimethyl-	Coffee	Viani <i>et al.</i> (1965) Reymond <i>et al.</i> (1966) Bondarovich <i>et al.</i> (1967) Goldman <i>et al.</i> (1967) Stoffelsma <i>et al.</i> (1968)	
	Filberts (roasted)	Sheldon <i>et al.</i> (1972)	
	Nonfat dry milk (stale)	Ferretti and Flanagan (1972)	
	Peanuts (roasted)	Mason <i>et al.</i> (1966) Johnson <i>et al.</i> (1971) Walradt <i>et al.</i> (1971)	
	Pecans (roasted)	Wang and Odell (1972)	
	Popcorn	Walradt <i>et al.</i> (1970)	
	Potato (dehydrated)	Sapers <i>et al.</i> (1971)	
	Potato chips	Deck and Chang (1965) Buttery <i>et al.</i> (1971)	
	Rye crisp bread	von Sydow and Anjou (1969)	
	Soybeans (deep fat-fried)	Wilkens and Lin (1970)	
	Soy protein (hydrolyzed)	Manley and Fagerson (1970)	
	Whey (spray-dried)	Ferretti and Flanagan (1971a) (T)	
	Beef (shallow fried)	Watanabe and Sato (1971b)	
	Casein	Ferretti <i>et al.</i> (1970)	
	Cocoa products	Dietrich <i>et al.</i> (1964) Flament <i>et al.</i> (1967) van Praag <i>et al.</i> (1968)	
	2,3,5-Trimethyl-	Coffee	Bondarovich <i>et al.</i> (1967) Goldman <i>et al.</i> (1967) Stoffelsma <i>et al.</i> (1968)
		Nonfat dry milk (stale)	Ferretti and Flanagan (1972) (T)
		Peanuts (roasted)	Johnson <i>et al.</i> (1971) Walradt <i>et al.</i> (1971)
		Pecans (roasted)	Wang and Odell (1972)
		Potato chips	Buttery <i>et al.</i> (1971)
Soy protein (hydrolyzed)		Manley and Fagerson (1970)	
Tomato		Ryder (1966)	
Whey (spray-dried)		Ferretti and Flanagan (1971a) (T)	
Barley (roasted)		Wang <i>et al.</i> (1969) Collins (1971)	
Beef (boiled)		Liebich <i>et al.</i> (1972)	
Beef (shallow fried)		Watanabe and Sato (1971b)	
Beef fat (heated)		Watanabe and Sato (1971a)	
Cocoa products		Flament <i>et al.</i> (1967) Rizzi (1967) van Praag <i>et al.</i> (1968) Reineccius <i>et al.</i> (1972)	
2,3,5,6-Tetramethyl-		Coffee	Bondarovich <i>et al.</i> (1967) Goldman <i>et al.</i> (1967) Stoffelsma <i>et al.</i> (1968)
		Lactose-casein	Ferretti and Flanagan (1971b)
		Nonfat dry milk (stale)	Ferretti and Flanagan (1972)
		Peanuts (roasted)	Mason <i>et al.</i> (1966) Johnson <i>et al.</i> (1971) Walradt <i>et al.</i> (1971)
		Pecans (roasted)	Wang and Odell (1972)
		Popcorn	Walradt <i>et al.</i> (1970) (T)
		Potato (dehydrated)	Sapers <i>et al.</i> (1971) (T)
	Potato chips	Buttery <i>et al.</i> (1971)	
	Rye crisp bread	von Sydow and Anjou (1969)	
	Soybeans (deep fat-fried)	Wilkens and Lin (1970)	
	Soy protein (hydrolyzed)	Manley and Fagerson (1970) (T)	
	Whey (spray-dried)	Ferretti and Flanagan (1971a)	
	Beef (shallow fried)	Watanabe and Sato (1971b)	
	Cocoa products	Dietrich <i>et al.</i> (1964) Flament <i>et al.</i> (1967) Rizzi (1967) van Praag <i>et al.</i> (1968) Reineccius <i>et al.</i> (1972)	
	Coffee	Stoffelsma <i>et al.</i> (1968) (T)	

Table I (Continued)

Pyrazine	Food	Reference
2-Ethyl-	Lactose-casein	Ferretti and Flanagan (1971b)
	Natto	Kosuge <i>et al.</i> (1962)
	Peanuts (roasted)	Walradt <i>et al.</i> (1971)
	Soy protein (hydrolyzed)	Manley and Fagerson (1970)
	Beef (shallow fried)	Watanabe and Sato (1971b)
	Beef fat (heated)	Watanabe and Sato (1971a)
	Cocoa products	van Praag <i>et al.</i> (1968)
		Reineccius <i>et al.</i> (1972)
		Bondarovich <i>et al.</i> (1967)
		Goldman <i>et al.</i> (1967)
2-Ethyl-3-methyl-	Filberts (roasted)	Sheldon <i>et al.</i> (1972)
	Peanuts (roasted)	Johnson <i>et al.</i> (1971)
		Walradt <i>et al.</i> (1971)
	Potato chips	Buttery <i>et al.</i> (1971)
	Rye crisp bread	von Sydow and Anjou (1969)
	Barley (roasted)	Collins (1971)
	Coffee	Bondarovich <i>et al.</i> (1967)
		Goldman <i>et al.</i> (1967)
		Stoffelsma <i>et al.</i> (1968)
		Sheldon <i>et al.</i> (1972) (T) (NESR)
2-Ethyl-5-methyl-	Lactose-casein	Ferretti and Flanagan (1971b) (NESR)
	Peanuts (roasted)	Johnson <i>et al.</i> (1971) (T)
		Walradt <i>et al.</i> (1971)
	Potato chips	Buttery <i>et al.</i> (1971)
	Rye crisp bread	von Sydow and Anjou (1969)
	Soy protein (hydrolyzed)	Manley and Fagerson (1970)
	Barley (roasted)	Wang <i>et al.</i> (1969)
		Collins (1971)
		Watanabe and Sato (1971b)
		Watanabe and Sato (1971a)
2-Ethyl-6-methyl-	Cocoa products	Rizzi (1967)
		van Praag <i>et al.</i> (1968)
		Reineccius <i>et al.</i> (1972)
	Coffee	Bondarovich <i>et al.</i> (1967)
		Goldman <i>et al.</i> (1967)
		Stoffelsma <i>et al.</i> (1968)
	Filberts (roasted)	Sheldon <i>et al.</i> (1972)
	Nonfat dry milk (stale)	Ferretti and Flanagan (1972) (T)
	Peanuts (roasted)	Johnson <i>et al.</i> (1971)
		Mason <i>et al.</i> (1966)
2,5-Diethyl-	Pecans (roasted)	Walradt <i>et al.</i> (1971)
	Popcorn	Wang and Odell (1972)
	Potato chips	Walradt <i>et al.</i> (1970)
	Soybeans (deep fat-fried)	Buttery <i>et al.</i> (1971)
	Whey (spray-dried)	Wilkens and Lin (1970)
	Cocoa products	Ferretti and Flanagan (1971a) (T)
	Coffee	Reineccius <i>et al.</i> (1972)
		Bondarovich <i>et al.</i> (1967)
		Goldman <i>et al.</i> (1967)
		Stoffelsma <i>et al.</i> (1968)
2,6-Diethyl-	Nonfat dry milk (stale)	Ferretti and Flanagan (1972) (T)
	Peanuts (roasted)	Johnson <i>et al.</i> (1971)
		Walradt <i>et al.</i> (1971)
	Pecans (roasted)	Wang and Odell (1972)
	Potato chips	Buttery <i>et al.</i> (1971)
	Rye crisp bread	von Sydow and Anjou (1969)
	Whey (spray-dried)	Ferretti and Flanagan (1971a) (T)
	Cocoa products	van der Wal <i>et al.</i> (1971)
	Coffee	Goldman <i>et al.</i> (1967)
	Peanuts (roasted)	Walradt <i>et al.</i> (1971) (T) (NESR)
2,5-Dimethyl-3-ethyl-	Coffee	Bondarovich <i>et al.</i> (1967)
		Goldman <i>et al.</i> (1967)
		Buttery <i>et al.</i> (1971)
	Potato chips	Wang <i>et al.</i> (1969) (NESR)
	Barley (roasted)	Collins (1971)
		Liebich <i>et al.</i> (1972) (NESR)
	Beef (boiled)	Watanabe and Sato (1971b)
	Beef (shallow fried)	

Table I (Continued)

Pyrazine	Food	Reference
	Beef fat (heated)	Watanabe and Sato (1971a)
	Cocoa products	Flament <i>et al.</i> (1967) Rizzi (1967) van Praag <i>et al.</i> (1968) Reineccius <i>et al.</i> (1972)
	Coffee	Bondarovich <i>et al.</i> (1967) Goldman <i>et al.</i> (1967) Stoffelsma <i>et al.</i> (1968)
	Filberts (roasted)	Sheldon <i>et al.</i> (1972)
	Peanuts (roasted)	Mason <i>et al.</i> (1966) Johnson <i>et al.</i> (1971) Walradt <i>et al.</i> (1971)
	Pecans (roasted)	Wang and Odell (1972)
	Popcorn	Walradt <i>et al.</i> (1970)
	Potato (dehydrated)	Sapers <i>et al.</i> (1971) (T) (NESR)
	Potato chips	Buttery <i>et al.</i> (1971)
	Rye crisp bread	von Sydow and Anjou (1969)
	Soybeans (deep fat-fried)	Wilkens and Lin (1970)
	Soy protein (hydrolyzed)	Manley and Fagerson (1970)
2,6-Dimethyl-3-ethyl-	Barley (roasted)	Collins (1971)
	Cocoa products	Rizzi (1967)
	Coffee	Goldman <i>et al.</i> (1967) Stoffelsma <i>et al.</i> (1968)
	Filberts (roasted)	Sheldon <i>et al.</i> (1972)
	Peanuts (roasted)	Johnson <i>et al.</i> (1971) (T) Walradt <i>et al.</i> (1971)
	Potato chips	Buttery <i>et al.</i> (1971)
	Soy protein (hydrolyzed)	Manley and Fagerson (1970)
2,3-Dimethyl-5-ethyl-	Cocoa products	van Praag <i>et al.</i> (1968)
2-Ethyl-3,5,6-trimethyl-	Cocoa products	Flament <i>et al.</i> (1967) van Praag <i>et al.</i> (1968)
	Coffee	Stoffelsma <i>et al.</i> (1968)
	Lactose-casein	Ferretti and Flanagan (1971b) (T)
	Peanuts (roasted)	Johnson <i>et al.</i> (1971) (T)
	Soy protein (hydrolyzed)	Manley and Fagerson (1970)
3,5-Diethyl-2,6-dimethyl-	Cocoa products	van der Wal <i>et al.</i> (1968)
3,6-Diethyl-2,5-dimethyl-	Cocoa products	van der Wal <i>et al.</i> (1968)
	Peanuts (roasted)	Walradt <i>et al.</i> (1971) (NESR)
2,5-Diethyl-3-methyl-	Filberts (roasted)	Sheldon <i>et al.</i> (1972) (T)
	Lactose-casein	Ferretti and Flanagan (1971b) (T)
2,6-Diethyl-3-methyl-	Beef (shallow fried)	Watanabe and Sato (1971b)
	Coffee	Bondarovich <i>et al.</i> (1967)
	Filberts (roasted)	Sheldon <i>et al.</i> (1972) (T)
	Peanuts (roasted)	Johnson <i>et al.</i> (1971) (T)
2,3-Diethyl-5-methyl-	Coffee	Bondarovich <i>et al.</i> (1967) Stoffelsma <i>et al.</i> (1968)
	Peanuts (roasted)	Walradt <i>et al.</i> (1971)
	Potato chips	Buttery <i>et al.</i> (1971)
2-Vinyl-	Coffee	Bondarovich <i>et al.</i> (1967)
	Peanuts (roasted)	Goldman <i>et al.</i> (1967)
	Rye crisp bread	von Sydow and Anjou (1969)
2-Methyl-5-vinyl-	Coffee	Bondarovich <i>et al.</i> (1967) Goldman <i>et al.</i> (1967)
	Peanuts (roasted)	Walradt <i>et al.</i> (1971)
	Potato chips	Buttery <i>et al.</i> (1971)
	Whey (spray-dried)	Ferretti and Flanagan (1971a) (T)
2-Methyl-6-vinyl	Coffee	Bondarovich <i>et al.</i> (1967) Goldman <i>et al.</i> (1967)
	Peanuts (roasted)	Walradt <i>et al.</i> (1971)
	Potato chips	Buttery <i>et al.</i> (1971) (T)
	Rye crisp bread	von Sydow and Anjou (1969)
	Whey (spray-dried)	Ferretti and Flanagan (1971a) (T)
Ethylvinyl-	Peanuts (roasted)	Johnson <i>et al.</i> (1971) (T) (NESR)
2,5-Dimethyl-3-vinyl-	Potato chips	Buttery <i>et al.</i> (1971) (T)
2-Propyl-	Coffee	Bondarovich <i>et al.</i> (1967) Goldman <i>et al.</i> (1967)

Table 1 (Continued)

Pyrazine	Food	Reference
	Peanuts (roasted)	Walradt <i>et al.</i> (1971)
	Rye crisp bread	von Sydow and Anjou (1969)
2-Methyl-6-propyl-	Peanuts (roasted)	Johnson <i>et al.</i> (1971) (T) Walradt <i>et al.</i> (1971) (NESR)
	Cocoa products	van der Wal <i>et al.</i> (1971) (NESR)
Isopropyl-	Peanuts (roasted)	Walradt <i>et al.</i> (1971) (T) (NESR)
2-Methyl-5-isopropyl-	Coffee	Bondarovich <i>et al.</i> (1967) Goldman <i>et al.</i> (1967)
	Peanuts (roasted)	Walradt <i>et al.</i> (1971) (NESR)
2-Methyl-6-isopropyl-	Coffee	Goldman <i>et al.</i> (1967)
2,5-Dimethyl-3-propyl-	Cocoa products	Flament <i>et al.</i> (1967)
2,5-Dimethyl-6-isopropyl-	Cocoa products	Flament <i>et al.</i> (1967) (NESR)
2-Propenyl-	Potato chips	Buttery <i>et al.</i> (1971) (T)
2-Methyl-5-propenyl-	Coffee	Bondarovich <i>et al.</i> (1967)
	Coffee	Bondarovich <i>et al.</i> (1967)
2-Methyl-6-propenyl-	Peanuts (roasted)	Walradt <i>et al.</i> (1971) (T) (NESR)
2-Isopropenyl-	Coffee	Bondarovich <i>et al.</i> (1967)
	Peanuts (roasted)	Johnson <i>et al.</i> (1971) (T)
Methylisopropenyl-		Walradt <i>et al.</i> (1971) (NESR)
2-Isobutyl-3-methyl-	Peanuts (roasted)	Johnson <i>et al.</i> (1971) (T) (NESR)
	Coffee	Goldman <i>et al.</i> (1967)
2-Isobutyl-3,6-dimethyl-	Potato chips	Buttery <i>et al.</i> (1971)
	Cocoa products	van der Wal <i>et al.</i> (1971)
2-Isoamyl-5-methyl-	Potato chips	Buttery <i>et al.</i> (1971)
6-Isoamyl-2-methyl-	Potato chips	Buttery <i>et al.</i> (1971) (T)
2-Isoamyl-3,6-dimethyl-	Cocoa products	van der Wal <i>et al.</i> (1968)
	Potato chips	Buttery <i>et al.</i> (1971) (T)
3-Isoamyl-2,6-dimethyl-	Cocoa products	Flament <i>et al.</i> (1967)
5-Isoamyl-2,3-dimethyl-	Cocoa products	van der Wal <i>et al.</i> (1968)
2-Isoamyl-3,5,6-trimethyl-	Cocoa products	Flament <i>et al.</i> (1967)
2-Isobutenyl-3-methyl-	Cocoa products	Flament <i>et al.</i> (1967)
Isobutenyldimethyl-	Potato chips	Buttery <i>et al.</i> (1971) (T)
Methylethylisobutyl-	Potato chips	Buttery <i>et al.</i> (1971) (T) (NESR)
2-Methyl-6-(2-methylbutyl)-	Potato chips	Buttery <i>et al.</i> (1971) (T) (NESR)
2-Methyl-6-(3-methylbutyl)-	Cocoa products	van der Wal <i>et al.</i> (1968)
2,5-Dimethyl-3-(2-methylbutyl)-	Cocoa products	van der Wal <i>et al.</i> (1971)
2,5-Dimethyl-3-(3-methylbutyl)-	Cocoa products	van der Wal <i>et al.</i> (1971)
2,6-Dimethyl-3-(3-methylbutyl)-	Cocoa products	van der Wal <i>et al.</i> (1971)
2,3-Dimethyl-5-(2-methylbutyl)-	Cocoa products	van der Wal <i>et al.</i> (1971)
3,5,6-Trimethyl-2-(2-methylbutyl)-	Cocoa products	Flament <i>et al.</i> (1967)
2-Acetyl-	Cocoa products	Flament <i>et al.</i> (1967)
	Peanuts (roasted)	Walradt <i>et al.</i> (1971)
	Popcorn	Walradt <i>et al.</i> (1970) (T)
	Potato chips	Buttery <i>et al.</i> (1971)
5-Acetyl-2-methyl-	Peanuts (roasted)	Walradt <i>et al.</i> (1971) (T)
6-Acetyl-2-methyl-	Peanuts (roasted)	Walradt <i>et al.</i> (1971) (T)
6-Acetyl-2-ethyl-	Peanuts (roasted)	Walradt <i>et al.</i> (1971)
3-Ethyl-2-methoxy-	Potato	Buttery <i>et al.</i> (1970) (T)
3-Isobutyl-2-methoxy-	Peppers (bell)	Buttery <i>et al.</i> (1969a,b)
	Peas (green)	Murray <i>et al.</i> (1970)
3-Isopropyl-2-methoxy-	Peas (green)	Murray <i>et al.</i> (1970)
3-s-Butyl-2-methoxy-	Peas (green)	Murray <i>et al.</i> (1970)
2-Methyl-6,7-dihydro-5H-cyclopenta-	Peanuts (roasted)	Walradt <i>et al.</i> (1971)
5-Methyl-6,7-dihydro-5H-cyclopenta-	Peanuts (roasted)	Walradt <i>et al.</i> (1971)
2(or 3),5-dimethyl-6,7-dihydro-5H-cyclopenta-	Peanuts (roasted)	Walradt <i>et al.</i> (1971)
Quinoxaline	Peanuts (roasted)	Walradt <i>et al.</i> (1971) (T)
5,6,7,8-Tetrahydroquinoxaline	Peanuts (roasted)	Walradt <i>et al.</i> (1971)

^a (T), tentative identification. (NESR), no exact structure reported.

sides sugars, other compounds, namely glycerol, acetaldehyde, glyoxal, 2,3-butanedione, hydroxyacetone, and glucosamine can react to form specific pyrazines. The au-

thors point out that the compound glucosamine contains the necessary carbon and nitrogen atoms needed to form a variety of alkylpyrazines.

Table II. Odor Thresholds and Flavor Properties of Synthesized Pyrazines^a

Compound	Odor threshold in water, ppb	Flavor description
2-Methoxy-3-isobutyl- ^b	0.002	Bell peppers
2-Methoxy-3-hexyl-	0.001	Bell peppers
2-Methoxy-3-propyl-	0.006	Bell peppers
2-Methoxy-3-isopropyl- ^c	0.002	Bell pepper-raw potato
2-Methoxy-3-ethyl- ^d	0.425	Raw potato
2-Methoxy-3-methyl-	4.0	Roasted peanuts
2-Methoxy-	700.0	Not characteristic
2-Isobutyl-3-methoxy-5-methyl-	0.260	Bell pepper-mint
2-Isobutyl-3-methoxy-6-methyl-	2.6	Minty-camphoraceous
2-Isobutyl-3-methoxy-5,6-dimethyl-	315.0	Minty-camphoraceous
2-Ethoxy-3-ethyl-	11.0	Raw potato
2,5-Dimethyl- ^e	1800.0	

^a Seifert *et al.* (1970, 1972). ^b Reported to be naturally present in bell peppers (Buttery *et al.*, 1969a,b) and green peas (Murray *et al.*, 1970). ^c Reported to be naturally present in green peas (Murray *et al.*, 1970). ^d Reported to be naturally present in potatoes (Buttery *et al.*, 1970). ^e Included for comparison.

The possibility of alkylpyrazine formation in foods as influenced by temperature of processing was discussed by Koehler and Odell (1970). At lower temperatures and over longer periods of time, the authors postulate that pyrazines can result from the reaction of sugars and amino acids to form a ditetrahydroxybutylpyrazine intermediate through condensation (Hough *et al.*, 1952) which then undergoes rearrangement and cleavage to form alkylpyrazines. However, at higher temperatures, immediate rearrangement and cleavage of sugars results in the formation of smaller hydroxycarbonyl and dicarbonyl fragments, which in turn can condense with amino acid nitrogen to also form alkylpyrazines.

Koehler and Odell (1970) also point out that products such as 2,3-butanedione, hydroxyacetone, and glyoxal can also be formed from lipid decomposition, and thus pyrazines can be formed from further lipid degradation upon heat processing.

The mechanism proposed by Wang *et al.* (1969) for the formation of acetyl and methyl acetylpyrazines involves the condensation of the browning reaction product *cis*-methyl reductone with glyoxal or pyruvaldehyde and amino acids.

Formation of alkenyl-substituted pyrazines may result through the dehydration of the corresponding hydroxypyrazines (Grimmett, 1965).

Walradt *et al.* (1971) have postulated that some of the dihydrocyclopentapyrazines that they reported isolating could form from the interaction of glyoxal and pyruvaldehyde with amino acids and the carbohydrate degradation product 2-hydroxy-3-methyl-2-cyclopenten-1-one.

In discussing the formation of pyrazines in processed soybeans, Wilkens and Lin (1970) postulated that the nitrogen source required for pyrazine formation came from thermal degradation of soy protein which was found to occur at temperatures above 190° (Kasarda and Black, 1968). However, the authors have overlooked the possibility of the nitrogen coming from free amino acids which may be present in processed soy products. Thus, pyrazine formation in soy products could also occur at temperatures well below 190° (Koehler and Odell, 1970; Reineccius *et al.*, 1972).

ISOLATION METHODS

A vast majority of the published procedures for isolating

Table III. Flavor Thresholds of Pyrazines Added to Dark Irish Beer^a

Compound	Flavor threshold, ^b ppm
Unsubstituted	>100
Methyl-	100
Ethyl-	10
2,5-Dimethyl-	25
2,6-Dimethyl-	3
2,3-Dimethyl-	50
Trimethyl-	1
2-Ethyl-5-methyl-	1
2-Ethyl-3-methyl-	2
2,5-Dimethyl-3-ethyl-	0.025
3,5-Dimethyl-2-ethyl-	0.025
Tetramethyl-	>100
2,5-Diethyl-3,6-dimethyl-	100

^a Collins (1971). ^b Minimum concentration of compound in beer which was detected by one-third of panel.

pyrazines from food systems start with some form of distillation. The process may be in the form of atmospheric steam distillation (Manley and Fagerson, 1970), vacuum steam distillation (Mason *et al.*, 1966), atmospheric solvent distillation (Koehler *et al.*, 1971), vacuum solvent distillation (Buttery *et al.*, 1969a,b), soaking (Collins, 1971), and heated headspace condensation (Walradt *et al.*, 1970). The distillation step is usually followed by concentration and then fractionation of the extract into an acidic fraction using HCl and then into the desired basic fraction using NaOH. The basic fraction is then normally extracted with a solvent and then concentrated before glc analysis. Solvents that have been used include dichloromethane (Manley and Fagerson, 1970), hexane (Buttery *et al.*, 1969a,b), pentane (Flament *et al.*, 1967), diethyl ether (Sapers *et al.*, 1971), and carbon disulfide (Wilkens and Lin, 1970).

Several limitations are evident with certain isolation procedures. For example, atmospheric steam distillation could actually result in the formation of pyrazines (Koehler and Odell, 1970), and also the treatment may represent a condition which is an unnatural step in the processing or preparation of the food as consumed.

Also, the use of solvents may cause denaturation of all or part of the food system, and thus the results do not actually reflect a naturally occurring food system.

Another serious limitation with most isolation procedures involves the treatment of a near neutral system with acidic and basic reagents. The acidic conditions could de-

Table IV. Odor Thresholds of Various Pyrazines in Water and Mineral Oil^a

Compound	Odor threshold, ppm ^b	
	Water	Mineral oil
2-Methyl-	105	27
2,5-Dimethyl-	35	17
2,6-Dimethyl-	54	8
2-Ethyl-	22	17
2,3,5-Trimethyl-	9	27
Monomethylmonoethyl-	0.5	0.9
2,3,5,6-Tetramethyl-	10	38
2,5-Dimethyl-3-ethyl-	43	24
2,6-Dimethyl-3-ethyl-	15	24
2- <i>n</i> -Pentyl-	1	9

^a Koehler *et al.* (1971). ^b Concentration which produced a positive response 50% of the time.

nature proteins, thus exposing reactive nitrogen groups, and the basic conditions could influence carbohydrate fragmentation. Thus, the manipulation of pH could actually be inducing the formation of pyrazines.

A relatively mild pyrazine isolation procedure has recently been reported by Reineccius *et al.* (1972). It involves the leaching of pyrazines and other compounds from a packed glass column of product with diethyl ether. However, the actual isolation of the basic fraction involves the characteristic acidic and basic treatments.

In light of the above limitations, it is suggested that a more concise picture of pyrazine types and amounts directly attributable to foods could be obtained by employing an isolation system as outlined by Schultz *et al.* (1971), whereby the volatiles from a sample are driven off with inert nitrogen and trapped onto a precolumn. Then through the use of a switching valve the volatiles are then separated and identified using glc-ms combinations. It should also be remembered that glc separation temperature conditions should not be at elevated levels due to possible pyrazine decomposition (Koehler and Odell, 1970).

It was not one of the primary objectives of this review to discuss the methods available for the synthesis of pyrazines. However, preparation of specific pyrazine compounds may be necessary to confirm identifications and to allow flavor evaluations to be made. For those specifically interested in pyrazine synthesis the following references are suggested: Krems and Spoerri (1947); Jones (1949); Klein and Spoerri (1950, 1951); Karmus and Spoerri (1952); Hirschberg and Spoerri (1961); Klein *et al.* (1964); Firmenich and Co. (1965); Firmenich *et al.* (1967); Grabowski *et al.* (1968); Seifert *et al.* (1970, 1972); Mookherjee and Klaiber (1972); and Nakel and Haynes (1972).

LITERATURE CITED

- Bondarovich, H. A., Friedel, P., Krampl, V., Renner, J. A., Shephard, F. W., Gianturco, M. A., *J. Agr. Food Chem.* **15**, 1093 (1967).
- Brandes, P., Strohr, C., *J. Prakt. Chem.* **54**, 481 (1896).
- Buttery, R. G., Seifert, R. M., Guadagni, D. G., Ling, L. C., *J. Agr. Food Chem.* **17**, 1322 (1969a).
- Buttery, R. G., Seifert, R. M., Guadagni, D. G., Ling, L. C., *J. Agr. Food Chem.* **19**, 969 (1971).
- Buttery, R. G., Seifert, R. M., Ling, L. C., *J. Agr. Food Chem.* **18**, 538 (1970).
- Buttery, R. G., Seifert, R. M., Lundin, R. E., Guadagni, D. G., Ling, L. C., *Chem. Ind.* **490** (1969b).
- Collins, E., *J. Agr. Food Chem.* **19**, 533 (1971).
- Davison, B. K., Wiggins, L. F., *Chem. Ind. (London)* **982** (1956).
- Dawes, I. W., Edwards, R. A., *Chem. Ind. (London)* **2203** (1966).
- Deck, R. E., Chang, S. S., *Chem. Ind. (London)* **1343** (1965).
- Dietrich, P., Lederer, E., Winter, M., Stoll, M., *Helv. Chim. Acta* **47**, 1581 (1964).
- Ferretti, A., Flanagan, V. P., *J. Agr. Food Chem.* **19**, 245 (1971a).
- Ferretti, A., Flanagan, V. P., *J. Dairy Sci.* **54**, 1769 (1971b).
- Ferretti, A., Flanagan, V. P., *J. Agr. Food Chem.* **20**, 695 (1972).
- Ferretti, A., Flanagan, V. P., Ruth, J. M., *J. Agr. Food Chem.* **18**, 13 (1970).
- Firmenich and Co., French Patent 1,391,212 (March 5, 1965).
- Firmenich, R., Firmenich, G., Firmenich, R. E., British Patent 1,061,734 (March 15, 1967).
- Flament, I., Willhalm, B., Stoll, M., *Helv. Chim. Acta* **50**, 2233 (1967).
- Goldman, I. M., Seibl, J., Flament, I., Gautschi, F., Winter, M., Willhalm, B., Stoll, M., *Helv. Chim. Acta* **50**, 694 (1967).
- Grabowski, E. J. J., Tristram, E. W., Tull, R., Pollak, P. I., *Tetrahedron Lett.* **5931** (1968).
- Grimmett, M. R., *Rev. Pure Appl. Chem.* **15**, 101 (1965).
- Guadagni, D. G., Buttery, R. G., Seifert, R. M., Venstrom, D. W., *J. Food Sci.* **36**, 363 (1971).
- Hirschberg, A., Spoerri, P. E., *J. Org. Chem.* **26**, 2356 (1961).
- Hodge, J. E., *J. Agr. Food Chem.* **1**, 928 (1953).
- Hodge, J. E., Mills, F. D., Fisher, B. E., *Cereal Sci. Today* **17**, 34 (1972).
- Hough, L., Jones, J. K. N., Richards, E. L., *J. Chem. Soc.* **3854** (1952).
- Irvine, J. C., Thomson, R. F., Garrett, C. S., *J. Chem. Soc.* **238** (1913).

- Johnson, B. R., Waller, G. R., Burlingame, A. L., *J. Agr. Food Chem.* **19**, 1020 (1971).
- Jones, R. G., *J. Amer. Chem. Soc.* **71**, 78 (1949).
- Karmus, G., Spoerri, P. E., *J. Amer. Chem. Soc.* **74**, 1580 (1952).
- Kasardá, D. D., Black, D. R., *Biopolymers* **6**, 1011 (1968).
- Klein, B., O'Donnell, E., Gordon, J. M., *J. Org. Chem.* **29**, 2623 (1964).
- Klein, B., Spoerri, P. E., *J. Amer. Chem. Soc.* **72**, 1844 (1950).
- Klein, B., Spoerri, P. E., *J. Amer. Chem. Soc.* **73**, 2949 (1951).
- Koehler, P. E., Mason, M. E., Newell, J. A., *J. Agr. Food Chem.* **17**, 393 (1969).
- Koehler, P. E., Mason, M. E., Odell, G. V., *J. Food Sci.* **36**, 816 (1971).
- Koehler, P. E., Odell, G. V., *J. Agr. Food Chem.* **18**, 895 (1970).
- Kosuge, T., Kamiya, H., *Nature (London)* **193**, 776 (1962).
- Kosuge, T., Kamiya, H., Adachi, T., *Yakugaku Zasshi* **82**, 190 (1962).
- Krems, I. J., Spoerri, P. E., *Chem. Rev.* **40**, 279 (1947).
- Liebich, H. M., Douglas, D. R., Zlatkis, A., Muggler-Chavan, F., Donzel, A., *J. Agr. Food Chem.* **20**, 96 (1972).
- Manley, C. H., Fagerson, I. S., *J. Agr. Food Chem.* **18**, 340 (1970).
- Marion, J. P., Muggler-Chavan, F., Viani, R., Bricout, J., Reymond, D., Egli, R. H., *Helv. Chim. Acta* **50**, 1509 (1967).
- Mason, M. E., Johnson, B., Hamming, M., *J. Agr. Food Chem.* **14**, 454 (1966).
- Mookherjee, B. D., Klaiber, E. M., *J. Org. Chem.* **37**, 511 (1972).
- Murray, K. E., Shipton, J., Whitfield, F. B., *Chem. Ind. (London)* **897** (1970).
- Nakel, G. M., Haynes, L. V., *J. Agr. Food Chem.* **20**, 682 (1972).
- Nakel, G. M., Hiler, G. D., U.S. Patent 3,619,210 (Nov 9, 1971).
- Newell, J. A., Mason, M. E., Matlock, R. S., *J. Agr. Food Chem.* **15**, 767 (1967).
- Polak's Frutal Works, British Patent 1,248,380 (Jan 26, 1972).
- Reichstein, T., Staudinger, H., British Patent No. 260,960 (Dec 24, 1928).
- Reineccius, G. A., Keeney, P. G., Weissberger, W. J., *J. Agr. Food Chem.* **20**, 202 (1972).
- Reymond, D., Muggler-Chavan, F., Viani, R., Vuataz, L., Egli, R. H., *J. Gas Chromatogr.* **4**, 28 (1966).
- Rizzi, G. P., *J. Agr. Food Chem.* **15**, 549 (1967).
- Roberts, D. L., U. S. Patent 3,402,051 (Sept 17, 1968).
- Ryder, W. S., *Advan. Chem Ser. no.* **56**, 87 (1966).
- Sapers, G. M., Osman, S. F., Dooley, C. J., Panasiuk, O., *J. Food Sci.* **36**, 93 (1971).
- Schultz, T. H., Flath, R. A., Mon, R., *J. Agr. Food Chem.* **19**, 1060 (1971).
- Seifert, R. M., Buttery, R. G., Guadagni, D. G., Black, D. R., Harris, J. G., *J. Agr. Food Chem.* **18**, 246 (1970).
- Seifert, R. M., Buttery, R. G., Guadagni, D. G., Black, D. R., Harris, J. G., *J. Agr. Food Chem.* **20**, 135 (1972).
- Sheldon, R. M., Lindsay, R. C., Libbey, L. M., *J. Food Sci.* **37**, 313 (1972).
- Smith, V. K., River, P., Kushner, S., U. S. Patent 2,677,686 (May 4, 1954).
- Stoffelsma, J., Sipma, G., Kettenes, D. K., Pypker, J., *J. Agr. Food Chem.* **16**, 1000 (1968).
- Takei, Y., Nakatani, Y., Kobayashi, A., Yamanishi, T., *Nippon Nogei Kagaku Kaishi* **43**, 667 (1969).
- van Praag, M., Bidmead, D. S., Canadian Patent 883,760 (Oct 19, 1971).
- van Praag, M., Stein, H. S., Tibbetts, M. S., *J. Agr. Food Chem.* **16**, 1005 (1968).
- van der Wal, B., Kettenes, D. K., Stoffelsma, J., Sipma, G., Semper, A. Th. J., *J. Agr. Food Chem.* **19**, 276 (1971).
- van der Wal, B., Sipma, G., Kettenes, D. K., Semper, A. Th. J., *Recl. Trav. Chim. Pays-Bas* **87**, 238 (1968).
- Viani, R., Muggler-Chavan, F., Reymond, D., Egli, R. H., *Helv. Chim. Acta* **48**, 1809 (1965).
- von Sydow, E., Anjou, K., *Lebensm. Wiss. Technol.* **2**, 15 (1969).
- Walradt, J. P., Lindsay, R. C., Libbey, L. M., *J. Agr. Food Chem.* **18**, 926 (1970).
- Walradt, J. P., Pittet, A. O., Kinlin, T. E., Muralidhara, R., Sanderson, A., *J. Agr. Food Chem.* **19**, 972 (1971).
- Wang, P., Kato, H., Fujimaki, M., *Agr. Biol. Chem.* **33**, 1775 (1969).
- Wang, P., Odell, G. V., *J. Agr. Food Chem.* **20**, 206 (1972).
- Watanabe, K., Sato, Y., *Agr. Biol. Chem.* **35**, 756 (1971a).
- Watanabe, K., Sato, Y., *J. Agr. Food Chem.* **19**, 1017 (1971b).
- Wiggins, L. F., Wise, W. S., *Chem. Ind. (London)* **656** (1955).
- Wilkins, W. F., Lin, F. M., *J. Agr. Food Chem.* **18**, 337 (1970).
- Wilson, R. A., Katz, I., *J. Agr. Food Chem.* **20**, 741 (1972).
- Winter, M., U. S. Patent 3,622,346 (Nov 23, 1971).
- Winter, M., Gautschi, F., Flament, I., Stoll, M., French Patent 1,530,436 (June 28, 1968).

Received for review May 9, 1972. Accepted September 13, 1972.