

- Moshonas, M. G.; Shaw, P. E. *J. Agric. Food Chem.* 1972, 20, 70.
 Moshonas, M. G.; Shaw, P. E. *J. Agric. Food Chem.* 1979, 27, 1337.
 Nordby, H. E.; Nagy, S. "Fruit and Vegetable Juice Processing Technology", 3rd ed.; Nelson, P. E.; Tressler, D. K., Eds.; Avi Publishing Co.: Westport, CT, 1980; Chapter 2, pp 63, 75-76.
 Redd, J. B., Intercit Laboratories, Inc., Safety Harbor, FL, personal communication, 1981.
 Shaw, P. E. "Citrus Science and Technology"; Nagy, S.; Shaw, P. E.; Veldhuis, M. K., Eds.; Avi Publishing Co.: Westport, CT, 1977a; Vol. 1, Chapter 11.
 Shaw, P. E. "Citrus Science and Technology"; Nagy, S.; Shaw, P. E.; Veldhuis, M. K., Eds.; Avi Publishing Co.: Westport, CT, 1977b; Vol. 1, Chapter 12.
 Wilson, C. W., III; Shaw, P. E. *J. Agric. Food Chem.* 1978, 26, 1430.
 Wilson, C. W., III; Shaw, P. E. *J. Agric. Food Chem.* 1981, 29, 494.
 Wolford, R. W.; Alberding, G. E.; Attaway, J. A. *J. Agric. Food Chem.* 1962, 10, 297.

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Isolation and Identification of Volatile Flavor Compounds in Fried Bacon

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Volatile flavor compounds were isolated from 120 lb of fried bacon by a specially designed apparatus. The isolated volatile flavor compounds were subjected to extensive gas chromatographic fractionation, and the pure fractions obtained were identified by infrared and mass spectrometry. A total of 135 compounds were identified. The compounds identified in the volatiles of fried bacon included hydrocarbons, alcohols, ketones, aldehydes, acids, esters, ethers, phenols, pyrazines, furans, thiazoles, oxazoles, oxazolines, pyrroles, pyridines, and miscellaneous compounds. Two interesting halogenated pyrroles, *N*-acetyl-2-chloropyrrole and *N*-acetyl-2-bromopyrrole, were synthesized to confirm the identification.

There have been a limited number of reports concerning the flavor constituents of cured pork and its related products. These reports (Cross and Ziegler, 1965; Langer et al., 1970; Lillard and Ayres, 1969; Ockerman et al., 1964) dealt exclusively with ham and sausage flavor constituents and resulted in the identification of a number of acids, alcohols, sulfur compounds, and, particularly, carbonyl compounds. On the other hand, extensive literature (Baltes et al., 1981; Fiddler et al., 1970a,b; Hamid and Saffle, 1965; Hruza et al., 1974; Kim et al., 1974; Kornreich and Issenberg, 1972; Lustre and Issenberg, 1969; Porter et al., 1965) exists on the comparison of sawdust smoke and liquid smoke (natural) flavors. Lustre and Issenberg (1970) studied the uptake of phenols from wood smoke in smoked pork belly. Knowles et al. (1975) reported the identification of 13 phenols, furfuryl alcohol, and cyclotene in the phenolic fraction of traditional kiln-smoked bacon. Most recently, Shu et al. (1980) identified 2,4,5-trimethyl-3(2*H*)-furanone from the phenolic fraction of the volatile flavor isolate of cooked Oscar Mayer bacon. However, literature on the systematic analysis of volatile

flavor constituents of cooked bacon is nonexistent.

The present paper reports the isolation and systematic characterization of the volatile flavor constituents of fried bacon.

EXPERIMENTAL SECTION

Isolation of the Volatile Compounds from Fried Bacon. The bacon used for this study was Oscar Mayer bacon ($1/8$ in. thick slices, 1 lb/package) purchased from a local supermarket.

Bacon was pan fried at 350 °C for 5 min to a golden yellow color. The volatile flavor compounds of fried bacon were isolated by the apparatus previously described by Chang et al. (1977). Nitrogen gas was used to remove the volatile compounds from the fried bacon. The samples and nitrogen gas were kept at 65 °C during the isolation period. Twenty pounds of fried bacon was used for each isolation which lasted 48 h. A total of six isolations were run. The total volatile isolate collected in traps cooled with dry ice and acetone was treated in a manner similar to that described by Herz and Chang (1966). The condensate was saturated with NaCl and extracted with anhydrous ethyl ether. The ether extract was dried with anhydrous sodium sulfate and then concentrated down to a final volume of 3 mL with the use of 30-plate Oldershaw column and a 200-plate spinning band still.

Fractionation of the Flavor Isolate. The fried bacon flavor isolate was fractionated in a manner similar to that described by Coleman et al. (1981). The initial preparative chromatography of the fried bacon flavor isolate was performed on a Beckman GC-5 gas chromatograph equipped with a thermal conductivity detector, fitted with

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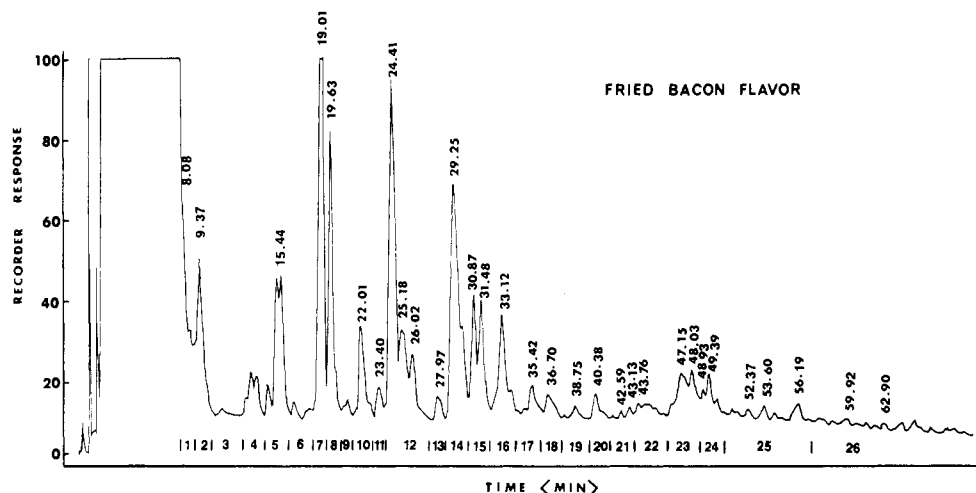


Figure 1. Gas chromatographic fraction of fried bacon flavor.

a $1/8$ in. o.d. \times 12 ft stainless steel column packed with 10% OV-17 on 60–80-mesh Chromosorb W. The flow rate was 30 mL/min with a column temperature which was held at 40 °C for 5 min and then increased by 2.5 °C/min to a holding temperature of 215 °C. The chromatogram (Figure 1) was divided into 26 broad fractions. Each broad fraction was successfully collected according to the method of Thompson et al. (1978).

A second fractionation was performed on all 26 broad fractions by using a $1/8$ in. o.d. \times 12 ft stainless steel column packed with 10% SP-1000 on 60–80-mesh Chromosorb W. A third chromatography was performed on selected subfractions by using a 2 mm i.d. \times 6 ft glass column packed with 10% OV-101 on 60–80-mesh Chromosorb W.

Mass Spectrometry and Infrared Spectrometry. Mass spectrometry was performed on a Du Pont 21-490 mass spectrometer with a jet separator interfaced to a Varian Moduline 2700 gas chromatograph fitted with an FID detector and a $1/8$ in. o.d. \times 12 ft stainless steel column packed with 10% OV-101 on 60–80-mesh Chromosorb W. The ionization voltage of the mass spectrometer was 70 eV.

Each fraction in sufficient quantity for infrared spectroscopy was analyzed on a Beckman Acculab 4 infrared spectrophotometer.

Synthesis of *N*-Acetyl-2-chloropyrrole. *N*-Acetylpyrrole was prepared by the reaction of pyrrole with *N*-acetylimidazole, according to the method of Reddy (1965).

To 0.49 g (4.50 mmol) of *N*-acetylpyrrole in 20 mL of diethyl ether at 0–5 °C, 0.67 g (5.00 mmol) of sulfuryl chloride in 10 mL of diethyl ether was added dropwise. After addition, the mixture was stirred for 5 h at 0–5 °C. To the reaction mixture, at room temperature, 10 mL of 10% sodium carbonate solution was added. The ethereal layer was separated and washed with water. The solution was dried over anhydrous sodium sulfate and the solvent removed with the use of a rotary evaporator. The analytical sample was purified by gas chromatography: colorless liquid; bp 98–102 °C/20 mmHg; MS data (Figure 2); IR 3440 (w), 3150 (m), 3010 (w), 1730 (s), 1600 (s), 1395 (m), 1375 (s), 1295 (s), 1220 (m), 1130 (m), 1110 (m), 1075 (m), 1050 cm^{-1} (m).

Synthesis of *N*-Acetyl-2-bromopyrrole. To 0.5 g (4.59 mmol) of *N*-acetylpyrrole in 20 mL of acetic acid at room temperature, 0.73 g (4.56 mmol) of bromine in 10 mL of acetic acid was added dropwise. After addition, the mixture was stirred for 12 h at 50–60 °C. To the reaction mixture, at room temperature, 200 mL of water was added.

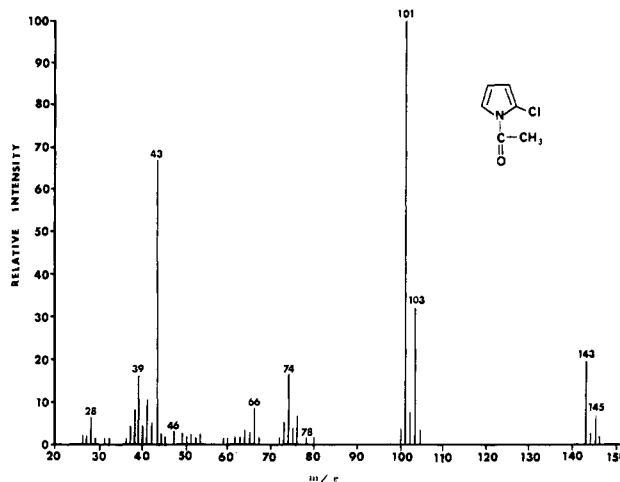


Figure 2. Mass spectrum of *N*-acetyl-2-chloropyrrole.

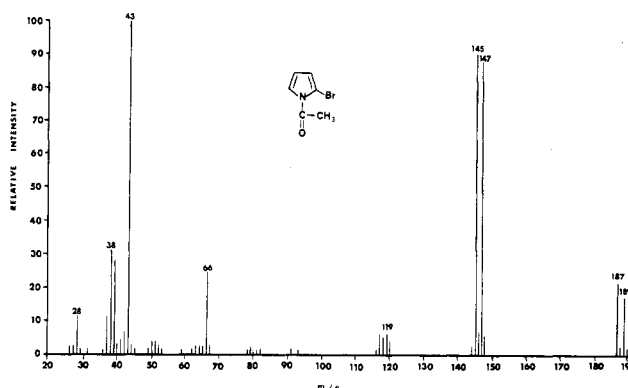


Figure 3. Mass spectrum of *N*-acetyl-2-bromopyrrole.

The aqueous solution was extracted with diethyl ether. The ethereal layer was washed with 5% of aqueous sodium carbonate solution and then washed with water. The ethereal solution was dried over anhydrous sodium sulfate and the solvent removed with the use of a rotary evaporator. The analytical sample was purified by gas chromatography: colorless liquid; bp 107–112 °C/20 mmHg; MS data (Figure 3); IR 3440 (w), 3150 (m), 3010 (w), 1730 (s), 1600 (m), 1460 (s), 1395 (s), 1370 (s), 1330 (s), 1295 (s), 1220 (m), 1170 (m), 1070 (s), 1040 cm^{-1} (w).

RESULTS AND DISCUSSION

A total of 135 compounds was identified in the volatile flavor isolated from 120 lb of fried bacon. Table I lists the

Table I. Volatile Constituents Identified in Bacon Flavor

fraction no. ^a	identifn	previously reported in		MS ref	IR identifn ^c
		pork ^b	smoke		
Hydrocarbons					
3-7	2-methylbutane			<i>i</i>	
4-4	3-methyl-3-ethylpentane			<i>i</i>	
3-12	heptane	+		<i>i</i>	+
4-11	octane	+		<i>i</i>	
11-2	undecane	+		<i>i</i>	
14-3	2,5-dimethylundecane			<i>i</i>	
12-2	dodecane	+		<i>i</i>	
15-2	2-methyldodecane			<i>i</i>	
15-3	tridecane			<i>i</i>	
20-3	4,8-dimethyltridecane			<i>i</i>	
18-1	tetradecane			<i>i</i>	
14-13	1-decyne			<i>i</i>	
6-3	toluene	+	<i>d</i>	<i>i</i>	+
9-8	1,2-dimethylbenzene		<i>e</i>	<i>i</i>	
12-5-4	isopropylbenzene			<i>k</i>	
12-10	1-methyl-4-ethylbenzene			<i>i</i>	
16-4-4	1,2-dimethyl-3-ethylbenzene			<i>i</i>	
19-15	<i>n</i> -pentylbenzene			<i>i</i>	
Alcohols					
1-3	ethanol	+	<i>d</i>	<i>i</i>	+
2-6	1-butanol	+		<i>i</i>	+
1-6	2-butanol	+		<i>j</i>	
5-9-1	1-pentanol	+		<i>i</i>	+
12-14-2	2,2-dimethyl-1-pentanol			<i>i</i>	
1-5	<i>tert</i> -amyl alcohol			<i>j</i>	
8-5	1-hexanol	+		<i>i</i>	+
13-12	2-ethyl-1-hexanol			<i>i</i>	
6-9-2	1-heptanol	+		<i>i</i>	
11-5	1-hepten-3-ol			<i>i</i>	+
14-17	1-octanol	+		<i>j</i>	
12-14-1	1-octen-3-ol	+		<i>j</i>	
12-23	1-octadecanol			<i>i</i>	
4-12	2-ethoxyethanol			<i>i</i>	
16-23	benzyl alcohol			<i>j</i>	+
17-4	2,3-dimethyl-2-hydroxy-3-phenylpropane			<i>k</i>	
Ketones					
4-10	3-hydroxy-2-butanone	+	<i>e</i>	<i>i</i>	
4-7	3-methyl-3-buten-2-one	+	<i>d</i>	<i>i</i>	
5-6	<i>trans</i> -3-penten-2-one	+		<i>i</i>	
11-7	3-hexanone		<i>f</i>	<i>i</i>	
4-1	5-methyl-2-hexanone			<i>i</i>	
9-4-1	2-heptanone	+		<i>i</i>	+
15-4	2,5-heptanedione			<i>i</i>	
2-1	7-methyl-4-octanone			<i>k</i>	
13-7	1,3-pentanedione			<i>i</i>	
15-16	2,3-dimethylcyclopent-2-en-1-one	+	<i>e</i>	<i>l</i>	
16-21	2-hydroxy-3-methyl-2-cyclopenten-1-one (cyclotene)		<i>g</i>	<i>i</i>	+
Aldehydes					
1-1-1	2-methylpropanal	+	<i>f</i>	<i>k</i>	
1-2	2-methylbutanal	+		<i>i</i>	
3-1	3-methylbutanal	+	<i>f</i>	<i>i</i>	
1-12	2-methylpentanal			<i>i</i>	
5-3-1	hexanal	+		<i>i</i>	+
9-3	heptanal	+			+
12-5	undecanal	+		<i>i</i>	
18-7	benzaldehyde	+	<i>d</i>	<i>i</i>	+
Ethers					
1-2-1	allyl ethyl ether			<i>i</i>	
4-5	butyl ethyl ether			<i>i</i>	
2-4	1,1-diethoxy-3-methylbutane			<i>i</i>	
Esters					
4-3	<i>n</i> -pentyl formate			<i>j</i>	
6-2	ethyl acetate	+		<i>j</i>	+
7-8	<i>n</i> -pentyl acetate	+		<i>j</i>	
8-5	isopentyl acetate			<i>j</i>	
8-7	<i>tert</i> -pentyl acetate			<i>i</i>	
12-3	2-acetoxy-2-butene			<i>k</i>	
6-4	acetoxyacetone			<i>i</i>	

Table I (Continued)

fraction no. ^a	identifn	previously reported in		MS ref	IR identifn ^c
		pork ^b	smoke		
Acids					
4-19	acetic acid	+	<i>e</i>	<i>i</i>	+
3-13	pentanoic acid	+	<i>d</i>	<i>i</i>	+
3-14	2-methylbutanoic acid		<i>d</i>	<i>i</i>	
12-4	heptanoic acid	+	<i>h</i>	<i>i</i>	+
Phenols					
14-23	phenol	+	<i>d</i>	<i>j</i>	+
16-26	2-methylphenol (<i>o</i> -cresol)		<i>e</i>	<i>i</i>	
18-9	3-methylphenol (<i>m</i> -cresol)		<i>d</i>	<i>i</i>	+
17-29	4-methylphenol (<i>p</i> -cresol)		<i>d</i>	<i>j</i>	
20-9	3,5-dimethylphenol (3,5-xyleneol)		<i>e</i>	<i>i</i>	
17-24	2-methoxyphenol (guaiacol)		<i>d</i>	<i>i</i>	
20-18	4-methyl-2-methoxyphenol (4-methylguaiacol)		<i>d</i>	<i>l</i>	
26-6	4-hydroxy-3-methoxyacetophenone (acetovanillone)		<i>e</i>	<i>i</i>	
25-15	3-methoxy-4-hydroxybenzoic acid			<i>k</i>	
8-4-2	<i>p</i> -chlorophenol			<i>i</i>	
Pyrazines					
4-11	pyrazine	+	<i>e</i>	<i>j</i>	
8-4	methylpyrazine	+	<i>e</i>	<i>j</i>	
11-3	2,3-dimethylpyrazine	+		<i>j</i>	
11-2	2,5-dimethylpyrazine	+	<i>e</i>	<i>j</i>	+
13-8	2,6-dimethylpyrazine	+	<i>e</i>	<i>m</i>	
12-10-1	trimethylpyrazine	+		<i>j</i>	
14-9-1	2-ethyl-3-methylpyrazine			<i>m</i>	
13-10	2-ethyl-5-methylpyrazine	+		<i>m</i>	
14-8-4	2-ethyl-6-methylpyrazine	+		<i>m</i>	
15-6-1	2-ethyl-6-vinylpyrazine			<i>m</i>	
20-6	2-acetyl-3-methylpyrazine			<i>m</i>	
18-6	2-acetyl-5-methylpyrazine	+		<i>m</i>	
9-6	tetramethylpyrazine	+		<i>j</i>	
15-12	2,5-diethylpyrazine	+		<i>m</i>	
16-6-2	2,3-dimethyl-5-ethylpyrazine	+		<i>m</i>	
16-5-1	2,5-dimethyl-3-ethylpyrazine	+		<i>m</i>	
18-3-1	2,3-diethyl-5-methylpyrazine	+		<i>m</i>	
18-3-2	2,5-diethyl-3-methylpyrazine	+		<i>m</i>	
18-4	3,5-diethyl-2-methylpyrazine	+		<i>m</i>	
18-3-2	2-ethyl-3,5,6-trimethylpyrazine			<i>m</i>	
17-11	2-isobutyl-3-methylpyrazine			<i>m</i>	
17-12	5,6,7,8-tetrahydroquinoxaline	+		<i>n</i>	
Furans					
12-11	2,4-dimethylfuran		<i>g</i>	<i>l</i>	
14-11	2,3,4-trimethylfuran			<i>k</i>	
13-5	2-butylfuran	+		<i>j</i>	
12-5-5	2-pentylfuran	+		<i>j</i>	
11-6	2-acetylfuran	+	<i>d</i>	<i>j</i>	+
11-8	furfuryl alcohol	+	<i>e</i>	<i>j</i>	
11-2	furfural	+	<i>e</i>	<i>j</i>	+
11-12	furan-3-aldehyde			<i>k</i>	
16-11	2-acetyl-5-methylfuran		<i>e</i>	<i>l</i>	
13-19	furoic acid			<i>i</i>	
16-4-10	ethyl 2-furoate	+		<i>j</i>	
7-5-1	2-methyltetrahydrofuran-3-one	+	<i>e</i>	<i>k</i>	
Thiazoles					
17-9	2-isopropyl-4,5-dimethylthiazole			<i>j</i>	
19-3	2-butyl-4,5-dimethylthiazole			<i>j</i>	
16-4-4	2,5-dimethyl-4-ethylthiazole			<i>l</i>	
Oxazoles and Oxazolines					
4-9	4,5-dimethyloxazole			<i>i</i>	
14-8-3	2-isopropyl-4,5-dimethyloxazole			<i>j</i>	
5-6	2,4-dimethyl-3-oxazoline			<i>o</i>	
Pyrroles					
12-9	5-methyl-2-formylpyrrole	+		<i>p</i>	
18-11	<i>N</i> -methyl-2-formylpyrrole			<i>l</i>	
19-10	2-acetylpyrrole	+	<i>g</i>	<i>p</i>	+
18-10	<i>N</i> -acetyl-2-chloropyrrole			Figure 2	
19-11	<i>N</i> -acetyl-2-bromopyrrole			Figure 3	
20-17	indole				
Pyridines					
5-7	pyridine			<i>l</i>	
7-2	2-methylpyridine			<i>l</i>	
7-4	4-methylpyridine			<i>l</i>	
17-26	3-methoxypyridine			<i>k</i>	

Table I (Continued)

fraction no. ^a	identifn	previously reported in		MS ref	IR identifn ^c
		pork ^b	smoke		
Miscellaneous Compounds					
4-6	4-methylpentanitriole				<i>k</i>
3-11	butyl isocyanate				<i>k</i>
20-11	<i>p</i> -methoxythioanisole				<i>k</i>
13-6	dichlorobenzene				<i>k</i>
15-1	3-aminopentane				<i>k</i>
12-10-1	bromotrichloromethane				<i>k</i>
20-24	dibutylphthalate				<i>k</i>
4-16	2,4,6-trimethyl-1,3,5-trioxane				<i>j</i>

^a The first, second, and third numerals indicate the position of the GC fraction during the first, second, and third chromatographies, respectively. ^b Van Straten (1977). ^c Pouchert (1978). ^d Hruza et al. (1974). ^e Kim et al. (1974). ^f Love and Bratzler (1966). ^g Baltes and Söchtig (1979). ^h Porter et al. (1965). ⁱ Heller and Milne (1978). ^j Jennings and Shibamoto (1980). ^k MSDC (1974). ^l ten Noever de Brauw et al. (1980). ^m Maga and Sizer (1973). ⁿ Pittet et al. (1974). ^o Mussinan et al. (1976). ^p Kinlin et al. (1972).

compounds identified. The identifications were primarily based on mass spectral data; the infrared data were used to aid the identification whenever samples were large enough to obtain the infrared spectra.

Hydrocarbons, Alcohols, and Carbonyl Compounds. Besides some Strecker aldehydes like 3-methylbutanal, most of the hydrocarbons, alcohols, and carbonyl compounds are probably not primary contributors to the flavor of bacon. 3-Hydroxy-2-butanone identified in bacon flavor occurs frequently in food aromas and is considered to provide a buttery note to cooked meat (Hirai et al., 1973).

2-Hydroxy-3-methyl-2-cyclopenten-1-one, which is also known as "cyclotene" or "maple lactone" is characterized by a burnt sugar odor impression (Ohloff and Flament, 1979). Cyclotene is a known product of Maillard reaction (Tressel et al., 1979), has not yet been identified in heated meat, but has been reported in smoke condensate (Lustre and Issenberg, 1969). The origin of cyclotene in fried bacon flavor may be due to the smoking agent. Cyclotene is also a flavor enhancer and may have an important influence on bacon flavor even at low concentrations (Lustre and Issenberg, 1970).

Phenols. It is well established that a significant portion of smoke flavor has been associated with the phenolic compounds. It is interesting to note that phenol, guaiacol, and 4-methylguaiacol were among the major components found in wood smoke vapor (Kornreich and Issenberg, 1972). They were also found as the major constituents in the phenolic fraction of smoked bacon flavor (Knowles et al., 1975). The majority of the phenolic compounds identified in wood smoke flavor are considered to be generated by the pyrolysis of lignin (20–30%) in wood (Kim et al., 1974; Wasserman and Fiddler, 1969). The bacon used in this study was sawdust smoked instead of liquid smoke.

Pyrazines. Since the identification of 2,5-dimethylpyrazine in the volatiles of cocoa (Dietrich et al., 1964) and potato chips (Deck and Chang, 1965), pyrazines were uncovered as an extremely important class of flavor compounds in foods. As a rule, alkylpyrazines produce a roasted nut like sensory impression (Ohloff and Flament, 1978). A total of 22 pyrazines was identified in the volatile flavor constituents of fried bacon; 5 of them have not been previously reported in the volatiles of heated pork. The mechanisms by which pyrazines formed in food have been reviewed previously (Maga and Sizer, 1973; Shibamoto and Bernhard, 1977; Maga, 1982).

Furans. Twelve furans were identified in this study. Furans are mainly associated with a sweet, nutty, and caramel-like odor impression, and they could contribute to the overall odor of heated meat (Ohloff and Flament,

1978) and a partial softening of the smoke aromas of phenolic compounds in smoked meat (Kim et al., 1974). 2-Pentylfuran, presumably formed by autoxidation of linoleate (Ho et al., 1978), imparts a beany and grassy flavor when added to vegetable oil (Smouse and Chang, 1967). The organoleptic properties of ethyl 2-furoate are characterized as burnt, buttery, and vanilla-like (Ohloff and Flament, 1978). The formation pathways for furans in food flavor have been reviewed recently (Maga, 1979).

Thiazoles, Oxazoles, and Oxazolines. Three thiazoles, two oxazoles, and one oxazoline were identified in the volatile flavor compounds isolated from fried bacon. Numerous thiazoles were reported in volatiles of a wide variety of foods such as heated beef (Chang and Peterson, 1977), cooked port liver (Mussinan and Walradt, 1974), coffee (Vitzthum and Werkhoff, 1974), baked potato (Coleman et al., 1981), and roasted peanuts (Lee et al., 1981). Alkylthiazoles have a green, nutty, and vegetable-like aroma. Thiazoles in foods may be formed as a result of interactions of sulfur-containing amino acids with carbohydrates or carbonyls.

The occurrence of oxazoles in foods has been reviewed (Maga, 1981a). Most recently, oxazoles had been identified in baked potato (Coleman et al., 1981) and roasted peanuts (Lee et al., 1981; Ho et al., 1982). In the aroma of meat, only 2,4,5-trimethyloxazole (Chang and Peterson, 1977) and 2-methylbenzoxazole (Ohloff and Flament, 1978) had been reported. 4,5-Dimethyloxazole identified in fried bacon flavor had been found in the reaction mixture of L-cysteine and diacetyl (Ho and Hartman, 1982).

The first oxazoline, 2,4,5-trimethyl-3-oxazoline, was reported by Chang et al. (1968) in the favor of boiled beef. So far, oxazolines have been found to occur only in meat (Ohloff and Flament, 1978) and peanut aroma (Ho et al., 1982). 2,4-Dimethyl-3-oxazoline found in fried bacon favor had been tentatively identified in the volatile flavor compounds of cooked beef (Mussinan et al., 1976) and was described as nutty and vegetable-like.

Pyrroles. Six pyrroles were identified in the volatiles of fried bacon. 2-Acetylpyrrole was previously identified in beef stew (Peterson et al., 1975) and was described as having a rather unpleasant plastic, antiseptic odor.

Two interesting pyrroles identified in this study were *N*-acetyl-2-chloropyrrole and *N*-acetyl-2-bromopyrrole. The structure of these two compounds were confirmed through synthesis of the authentic compounds. The mass spectrum of the authentic *N*-acetyl-2-chloropyrrole (Figure 2) matched well with that of the isolated compound. The ratio of the *m/e* 145 ion to the *m/e* 143 ion was calculated to be 31.6%, which clearly indicated the presence of a chlorine atom. The mass spectrum of the authentic *N*-

acetyl-2-bromopyrrole (Figure 3) also matched well with that of the isolated compound. The mass fragmentation mechanism of *N*-acetyl-2-bromopyrrole is very similar to that of *N*-acetyl-2-chloropyrrole.

Pyridines. Four pyridines were identified in the volatile flavor compounds of fried bacon. The importance of pyridine derivatives as aroma constituents has remained quite limited so far (Maga, 1981b). 2-Methylpyridine was described as an astringent and hazelnut-like odor.

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Registry No. 2-Methylbutane, 78-78-4; 3-methyl-3-ethylpentane, 1067-08-9; heptane, 142-82-5; octane, 111-65-9; undecane, 1120-21-4; 2,5-dimethylundecane, 17301-22-3; dodecane, 112-40-3; 2-methyldodecane, 1560-97-0; tridecane, 629-50-5; 4,8-dimethyltridecane, 55030-62-1; tetradecane, 544-76-3; 1-decyne, 764-93-2; toluene, 108-88-3; 1,2-dimethylbenzene, 95-47-6; isopropylbenzene, 98-82-8; 1-methyl-4-ethylbenzene, 622-96-8; 1,2-dimethyl-3-ethylbenzene, 933-98-2; *n*-pentylbenzene, 538-68-1; ethanol, 64-17-5; 1-butanol, 71-36-3; 2-butanol, 78-92-2; pyrazine, 290-37-9; methylpyrazine, 109-08-0; 2,3-dimethylpyrazine, 5910-89-4; 2,5-dimethylpyrazine, 123-32-0; 2,6-dimethylpyrazine, 108-50-9; trimethylpyrazine, 14667-55-1; 2-ethyl-3-methylpyrazine, 15707-23-0; 2-ethyl-5-methylpyrazine, 13360-64-0; 2-ethyl-6-methylpyrazine, 13925-03-6; 2-ethyl-6-vinylpyrazine, 32736-90-6; 2-acetyl-3-methylpyrazine, 23787-80-6; 2-acetyl-5-methylpyrazine, 22047-27-4; tetramethylpyrazine, 1124-11-4; 2,5-diethylpyrazine, 13238-84-1; 2,3-dimethyl-5-ethylpyrazine, 15707-34-3; 2,5-dimethyl-3-ethylpyrazine, 13360-65-1; 2,3-diethyl-5-methylpyrazine, 18138-04-0; 2,5-diethyl-3-methylpyrazine, 32736-91-7; 3,5-diethyl-2-methylpyrazine, 18138-05-1; 2-ethyl-3,5,6-trimethylpyrazine, 17398-16-2; 2-isobutyl-3-methylpyrazine, 13925-06-9; 5,6,7,8-tetrahydroquinoxaline, 34413-35-9; 2,4-dimethylfuran, 3710-43-8; 2,3,4-trimethylfuran, 10599-57-2; 2-butylfuran, 4466-24-4; 2-pentylfuran, 3777-69-3; 2-acetylfuran, 1192-62-7; furfuryl alcohol, 98-00-0; furfural, 98-01-1; furan-3-aldehyde, 498-60-2; 2-acetyl-5-methylfuran, 1193-79-9; furoic acid, 26447-28-9; ethyl 2-furoate, 614-99-3; 2-methyltetrahydrofuran-3-one, 3188-00-9; 1-pentanol, 71-41-0; 2,2-dimethyl-1-pentanol, 2370-12-9; *tert*-amyl alcohol, 75-85-4; 1-hexanol, 111-27-3; 2-ethyl-1-hexanol, 104-76-7; 1-heptanol, 111-70-6; 1-hepten-3-ol, 4938-52-7; 1-octanol, 111-87-5; 1-octen-3-ol, 3391-86-4; 1-octadecanol, 112-92-5; 2-ethoxyethanol, 110-80-5; benzyl alcohol, 100-51-6; 2,3-dimethyl-2-hydroxy-3-phenylpropane, 3280-08-8; 3-hydroxy-2-butanone, 513-86-0; 3-methyl-3-buten-2-one, 814-78-8; *trans*-3-penten-2-one, 3102-33-8; 3-hexanone, 589-38-8; 5-methyl-2-hexanone, 110-12-3; 2-heptanone, 110-43-0; 2,5-heptanedione, 1703-51-1; 7-methyl-4-octanone, 20809-46-5; 1,3-pentanedione, 623-38-1; 2,3-dimethylcyclopent-2-en-1-one, 1121-05-7; cyclotene, 80-71-7; 2-methylpropanal, 78-84-2; 2-methylbutanal, 96-17-3; 3-methylbutanal, 590-86-3; 2-methylpentanal, 123-15-9; hexanal, 66-25-1; heptanal, 111-71-7; undecanal, 112-44-7; benzaldehyde, 100-52-7; allyl ethyl ether, 557-31-3; butyl ethyl ether, 628-81-9; 1,1-diethoxy-3-methylbutane, 3842-03-3; 2-isopropyl-4,5-dimethylthiazole, 53498-30-9; 2-butyl-4,5-dimethylthiazole, 76572-48-0; 2,5-dimethyl-4-ethylthiazole, 32272-57-4; 4,5-dimethylloxazole, 20662-83-3; 2-isopropyl-4,5-dimethylloxazole, 19519-45-0; 2,4-dimethyl-3-oxazoline, 77311-02-5; 5-methyl-2-formylpyrrole, 1192-79-6; *N*-methyl-2-formylpyrrole, 1192-58-1; 2-acetylpyrrole, 1072-83-9; *N*-acetyl-2-chloropyrrole, 84455-05-0; *N*-acetyl-2-bromopyrrole, 84455-06-1; indole, 120-72-9; phenol, 108-95-2; *o*-cresol, 95-48-7; *m*-cresol, 108-39-4; *p*-cresol, 106-44-5; 3,5-xyleneol, 108-68-9; guaiacol, 90-05-1; 4-methylguaiacol, 93-51-6; acetovanillone, 498-02-2; 3-methoxy-4-hydroxybenzoic acid, 121-34-6; *p*-chlorophenol, 106-48-9; 4-methylpentanitrile, 542-54-1; butyl isocyanate, 111-36-4; *p*-methoxythioanisole, 1879-16-9; dichlorobenzene, 25321-22-6; 3-aminopentane, 616-24-0; bromotrichloromethane, 75-62-7; dibutyl phthalate, 84-74-2; 2,4,6-trimethyl-1,3,5-trioxane, 123-63-7; 1-pentyl formate, 638-49-3; ethyl acetate, 141-78-6; *n*-pentyl acetate, 628-63-7; isopentyl acetate, 123-92-2; *tert*-pentyl acetate, 625-16-1; 2-acetoxy-2-butene, 6203-88-9; acetoxyacetone, 592-20-1; pyridine, 110-86-1; 2-methylpyridine, 109-06-8; 4-methylpyridine, 108-89-4; 3-methoxy-pyridine, 7295-76-3; acetic acid, 64-19-7; pentanoic acid, 109-52-4; 2-methylbutanoic acid, 116-53-0; heptanoic acid, 111-

14-8; *N*-acetylpyrrole, 609-41-6.

LITERATURE CITED

- Baltes, W.; Söchtig, I. *Z. Lebensm.-Unters.-Forsch.* **1979**, *169*, 9.
- Baltes, W.; Wittkowski, R.; Söchtig, I.; Block, H.; Toth, L. In "The Quality of Food and Beverages"; Charalambous, G.; Inglett, G., Eds.; Academic Press: New York, 1981; Vol. 2, 1.
- Chang, S. S.; Hirai, C.; Reddy, B. R.; Herz, K. O.; Kato, A.; Sipma, G. *Chem. Ind. (London)* **1968**, 1639.
- Chang, S. S.; Peterson, R. J. *J. Food Sci.* **1977**, *42*, 298.
- Chang, S. S.; Vallese, F. M.; Hwang, L. S.; Hsieh, O. A.-L.; Min, D. B. S. *J. Agric. Food Chem.* **1977**, *25*, 450.
- Coleman, E. C.; Ho, C.-T.; Chang, S. S. *J. Agric. Food Chem.* **1981**, *29*, 42.
- Cross, C. K.; Ziegler, P. J. *J. Food Sci.* **1965**, *30*, 610.
- Deck, R. E.; Chang, S. S. *Chem. Ind. (London)* **1965**, 1343.
- Dietrich, P. E.; Lederer, M.; Winter, M.; Stoll, M. *Helv. Chim. Acta* **1964**, *47*, 1581.
- Fiddler, W.; Doerr, R. C.; Wassermann, A. E. *J. Agric. Food Chem.* **1970a**, *18*, 310.
- Fiddler, W.; Doerr, R. C.; Wassermann, A. E. *J. Agric. Food Chem.* **1970b**, *18*, 934.
- Hamid, H. A.; Saffle, R. L. *J. Food Sci.* **1965**, *30*, 697.
- Heller, S. R.; Milne, G. W. A. "EPA-NIH Mass Spectral Data Base"; U.S. Government Printing Office: Washington, DC, 1978.
- Herz, K. O.; Chang, S. S. *J. Food Sci.* **1966**, *31*, 937.
- Hirai, C.; Herz, K. O.; Pokorny, J.; Chang, S. S. *J. Food Sci.* **1973**, *38*, 393.
- Ho, C.-T.; Hartman, G. J. *J. Agric. Food Chem.* **1982**, *30*, 793.
- Ho, C.-T.; Lee, M.-H.; Chang, S. S. *J. Food Sci.* **1982**, *47*, 127.
- Ho, C.-T.; Smagula, M. S.; Chang, S. S. *J. Am. Oil Chem. Soc.* **1978**, *55*, 233.
- Hruza, D. E.; van Praag, M.; Heinsohn, H. *J. Agric. Food Chem.* **1974**, *22*, 123.
- Jennings, W.; Shibamoto, T. "Quantitative Analysis of Flavor and Fragrance Volatiles by Glass Capillary Gas Chromatography"; Academic Press: New York, 1980.
- Kim, K.; Kurata, T.; Fujimaki, M. *Agric. Biol. Chem.* **1974**, *38*, 53.
- Kinlin, T. E.; Muralidhara, R.; Pittet, A. O.; Sanderson, A.; Walradt, J. P. *J. Agric. Food Chem.* **1972**, *20*, 1021.
- Knowles, M. E.; Gilbert, J.; McWeeny, D. J. *J. Sci. Food Agric.* **1975**, *26*, 189.
- Kornreich, M. R.; Issenberg, P. J. *J. Agric. Food Chem.* **1972**, *20*, 1109.
- Langer, H. J.; Heckel, V.; Malek, E. *Fleischwirtschaft* **1970**, *50*, 1193.
- Lee, M.-H.; Ho, C.-T.; Chang, S. S. *J. Agric. Food Chem.* **1981**, *29*, 684.
- Lillard, D. A.; Ayres, J. C. *Food Technol. (Chicago)* **1969**, *23*, 251.
- Love, S.; Bratzler, L. J. *J. Food Sci.* **1966**, *31*, 218.
- Lustre, A. O.; Issenberg, P. J. *J. Agric. Food Chem.* **1969**, *17*, 1387.
- Lustre, A. O.; Issenberg, P. J. *J. Agric. Food Chem.* **1970**, *18*, 1056.
- Maga, J. A. *CRC Crit. Rev. Food Sci. Nutr.* **1979**, *10*, 355.
- Maga, J. A. *CRC Crit. Rev. Food Sci. Nutr.* **1981a**, *12*, 295.
- Maga, J. A. *J. Agric. Food Chem.* **1981b**, *29*, 895.
- Maga, J. A. *CRC Crit. Rev. Food Sci. Nutr.* **1982**, *13*, 1.
- Maga, J. A.; Sizer, C. E. *CRC Crit. Rev. Food Technol.* **1973**, *4*, 39.
- MSDC "Eight Peak Index of Mass Spectra", 2nd ed.; Mass Spectrometry Data Center: Reading, U.K., 1974.
- Mussinan, C. J.; Walradt, J. P. *J. Agric. Food Chem.* **1974**, *22*, 827.
- Mussinan, C. J.; Wilson, R. A.; Katz, I.; Hruza, A.; Vock, M. H. *ACS Symp. Ser.* **1976**, *No. 26*, 133.
- Ockerman, H. W.; Blumer, T. N.; Craig, H. B. *J. Food Sci.* **1964**, *29*, 123.
- Ohloff, G.; Flament, I. *Heterocycles* **1978**, *11*, 663.
- Ohloff, G.; Flament, I. *Fortschr. Chem. Org. Naturst.* **1979**, *36*, 231.
- Peterson, R. J.; Izzo, H. J.; Jungermann, E. Chang, S. S. *J. Food Sci.* **1975**, *40*, 948.
- Pittet, A. O.; Muralidhara, R.; Walradt, J. P.; Kinlin, T. *J. Agric. Food Chem.* **1974**, *22*, 273.

- Porter, R. W.; Bratzler, K. J.; Pearson, A. M. *J. Food Sci.* 1965, 30, 615.
- Pouchert, C. J. "The Aldrich Library of Infrared Spectra", 2nd ed.; Aldrich Chemical Co.: Milwaukee, WI, 1978.
- Reddy, G. S. *Chem. Ind. (London)* 1965, 1426.
- Shibamoto, T.; Bernhard, R. A. *J. Agric. Food Chem.* 1977, 25, 609.
- Shu, C. K.; Mookherjee, B. D.; Vock, M. H. U.S. Patent 4 234 616, Nov 18, 1980.
- Smouse, T. H.; Chang, S. S. *J. Am. Oil Chem. Soc.* 1967, 44, 509.
- ten Noever de Brauw, M. C.; Bouwman, J.; Tas, A. C.; LaVos, G. F. "Compilation of Mass Spectra of Volatile Compounds in Food"; TNO: Zeist, The Netherlands, 1980.
- Thompson, J. A.; May, W. A.; Paulose, M. M.; Peterson, R. J.; Chang, S. S. *J. Am. Oil Chem. Soc.* 1978, 55, 897.
- Tressel, R.; Grünewald, K. G.; Silwar, R.; Bahri, D. In "Progress in Flavor Research"; Land, D. G.; Nursten, H. E., Eds.; Applied Science: London, 1979; p 197.
- Van Straten, S. "Volatile Compounds in Food", 4th ed.; TNO: Zeist, The Netherlands, 1977.
- Vitzthum, O. G.; Werkhoff, P. *J. Food Sci.* 1974, 39, 1210.
- Wasserman, A. E.; Fiddler, W. *Proc. Meat. Ind. Res. Corp. Conf.* 1969, 163.

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The Browning Capacity of Grapes. 1. Changes in Polyphenol Oxidase Activities during Development and Maturation of the Fruit

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The investigation over a 3-year period of the development of polyphenol oxidase activities throughout the growth and maturation of five varieties of grape reveals the extreme complexity of the phenomenon from the green stage up until the full maturation of the fruit. Although they remain comparable, the crude total polyphenol oxidase activities and the solubilized polyphenol oxidase activities differ for certain years in the intensity and the speed of their development. The varietal factor appears to be important and characteristic in the case of the crude soluble polyphenol oxidase activities.

Browning during grape juice processing is a well-known phenomenon, the causes of which are essentially enzymatic in origin. In the presence of the oxygen in the air, the polyphenol oxidase of the grape (*o*-diphenol oxidase, EC 1.10.3.1) catalyses the oxidation of certain phenolic compounds occurring naturally in the fruit; the quinones thus formed lead by polymerization to the creation of brown pigments which are characteristic of the browning phenomenon.

This phenomenon causes a radical change in the color and the flavor and is thus a considerable handicap which greatly diminishes the quality of the processed products. It is therefore desirable to find ways of avoiding this, in particular by finding varieties having the lowest possible level of sensitivity to browning. This latter is in connection with many parameters—parameters which are often lacking in definition. Among those, both polyphenol oxidase and phenolic compounds levels play an important role. In that first part of work we have been interested in polyphenol oxidase. Data concerning phenolic compounds will be reported in a following paper. Quite a number of studies have been made concerning polyphenol oxidase in the grape (Mayer et al., 1965; Poux, 1966; Constantinides, 1967; Ivanov and Ivanova, 1968; Montedoro, 1969a,b; Montedoro and Cantarelli, 1969; Harel and Mayer, 1971; Lerner et al., 1972; Traverso-Rueda and Singleton, 1973; Dubernet and Ribéreau-Gayon, 1973; Harel et al., 1973; Dubernet, 1974; Dubernet and Ribéreau-Gayon, 1974; Lerner et al., 1974; Kidron et al.,

1977, 1978; Wissemann and Lee, 1980a,b).

In our research, we therefore started by studying the variations in polyphenol oxidase activities throughout the development and the maturation of a number of varieties and we compared the results obtained over several consecutive years.

MATERIALS AND METHODS

Plant Material. The study was carried out from 1979 to 1981 on a number of varieties from the same vineyard. In 1979, four varieties were selected for study throughout their development: two of these were known to be sensitive to browning (Grenache, a red variety and Clairette, a white variety) and two were known to resist browning (Cargnane, a red variety, and Ugni blanc, a white variety). To the results obtained in 1979 were added others obtained in 1980 and 1981 for most of the above varieties plus Maccabeo (white variety). Between July 1st and Sept 30th, four samplings were taken from each variety in 1979 and 19 samplings were taken in 1980. In 1981, 14 samplings were taken between June 20th and Sept 30th. In 1979 and 1980, the grapes sampled were freeze-dried immediately after being harvested. In 1981, they were analyzed fresh when picked. At the time of testing, the deseeded grapes are immersed in liquid nitrogen and ground immediately in a ball grinder (Dangoumau type) while still in the presence of liquid nitrogen. The powders obtained by this method are used for the preparation of enzymatic extracts.

Preparation of Enzymatic Extracts and Measurement of Polyphenol Oxidase Activity. To 5 g of the grape powder placed in suspension in 50 mL of 0.1 M phosphate buffer, pH 7.2, is added 400 mg of poly(ethylene glycol), 1.5 g of Polyclar AT (to set the phenolic compounds occurring naturally in the fruit) and 75 μ L of a solution of mercapto-2-ethanol at 10/100. After homogenization at 0 °C in an Ultra-Turax for 30 s and gentle agitation at 0 °C for 30 min, the mixture is centrifuged (40000g, 2 °C,

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