Volatile Components of the Phenolic Fraction of Cooked Bacon

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The volatile components of cooked bacon were isolated via vacuum steam distillation and chemical separation methods. The organoleptically significant phenolic fraction was analyzed, and 43 components were identified, of which five compounds were synthesized for confirmation of structures, including 2,4,5-trimethyl-3(2*H*)-furanone.

INTRODUCTION

Bacon is one of the major meat products. Bacon flavors are being used in various products such as bacon snacks, bacon bits, and bacon chips. A review of the literature revealed abundant information regarding the toxicology of nitrosamines (Mottram et al., 1977; Harvey et al., 1978) but very few investigations of volatile constituents (Knowles et al., 1975; Lustre and Issenber, 1970; Ho et al., 1983). Lustre and Issenberg (1970) identified 20 components including phenols, guaiacols, vanillin, cyclotene, and maltol from the phenolic fraction of baconlike strips, smoked bellies. Knowles et al. (1975) reported similar components from various smoked bacon samples. Both groups believed that the phenolic fraction played a very important role for bacon flavors. Ho et al. (1983) identified 135 compounds from the fried bacon including 10 phenolic compounds.

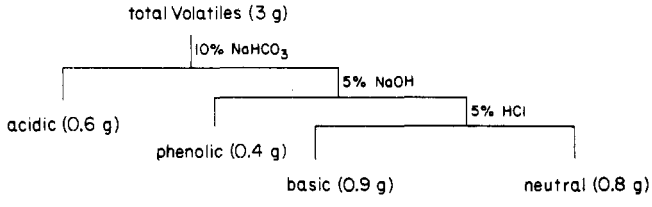
This laboratory has studied the volatiles from the cooked bacon. The isolations technique of volatiles and the identification of the constituents of phenolic fraction have been covered in a patent (Shu et al., 1980). This paper reports the procedure and the results of this analysis.

EXPERIMENTAL SECTION

Sample Preparation. Following a laboratory scale procedure, five 100-lb batches of Oscar Mayer bacon were each ground to $^3/_{16}$-in. mesh and then cooked for 1 h in a steam-jacketed kettle with refluxing from 20 °C rapidly to 175 °C. The slurry obtained, after combining batches, possessed the characteristic fried bacon odor.

Steam Distillation. The slurry was divided into 10 50-lb charges. Each charge was subjected to vacuum steam distillation for 16 h at 50 °C and 1 mmHg. Approximately 12 L of distillate were collected, saturated with NaCl, and extracted with diethyl ether for 3 days in a continuous extractor. The combined ether extracts were concentrated to ca. 1 L on a Kuderna–Danish concentrator. Approximately 3 g of volatiles was obtained from the initial 500 lb of bacon.

Chemical Separation. The ether extract (3 g) was chemically separated into acidic, phenolic, basic, and neutral fractions as follows:



These four fractions were evaluated by a flavor panel of two experienced flavorists for aroma and taste as follows: phenolic fraction, very characteristic for fried bacon in both aroma and taste, the best fraction; neutral fraction, fatty, green, pork rind, lard; basic fraction, ammonia-like, not

Table I. Volatile Components Identified from the Phenolic Fraction of Cooked Bacon

components	method[d]	ref
Phenols (8)		
phenol	IR	*a–c*
o-cresol	IR	*a*, *c*
m-cresol	IR	*a–c*
p-cresol	I_E	*b*, *c*
2-ethylphenol	IR, I_E	
4-ethylphenol	I_E	
2,6-dimethylphenol		
ionol		
Guaiacols (13)		
guaiacol	IR, I_E, NMR	*a–c*
4-methylguaiacol	IR, I_E, NMR	*a–c*
4-ethylguaiacol	IR, I_E, NMR	*b*, *c*
4-propylguaiacol	I_E, NMR, synth	*c*
4-isopropylguaiacol		
4-vinylguaiacol	IR, I_E	*b*, *c*
eugenol	I_E, NMR	*b*, *c*
cis-isoeugenol	I_E	*b*, *c*
trans-isoeugenol	I_E	*b*, *c*
6-methylguaiacol	I_E, synth	
6-ethylguaiacol		
vanillin	I_E	*b*
acetovanillone	I_E	*a*, *b*
2,6-Dimethoxyphenols (4)		
2,6-dimethoxyphenol	IR, I_E, NMR	*b*, *c*
4-methyl-2,6-dimethoxyphenol	I_E, NMR	*b*, *c*
4-ethyl-2,6-dimethoxyphenol	I_E, synth	*b*, *c*
4-propyl-2,6-dimethoxyphenol	I_E, synth	*c*
Lactones (8)		
γ-valerolactone	IR, I_E	
γ-hexalactone	I_E	
γ-nonalactone	I_E	
Δ-hexalactone		
Δ-heptalactone		
Δ-octalactone	I_E	
Δ-nonalactone	I_E	
2,4-methyl-2-butenolide	I_E	
Cyclo Diones (4)		
cyclotene	IR, I_E, NMR	*a–c*
3,5-dimethylcyclopentane-1,2-dione	I_E	
3,4-dimethylgyclopentane-1,2-dione	I_E	
3-ethylcyclopentane-1,2-dione	I_E	
Acids (5)		
acetic acid		*a*
propionic acid		
octanoic acid		
decanoic acid		
2-ethylhexanoic acid	IR, I_E, NMR	
Furanone (1)		
2,4,5-trimethyl-3(2*H*)-furanone	IR, I_E, NMR, synthesis	

[a] Ho et al., 1983. [b] Lustre and Issenberg, 1970. [c] Knowles et al., 1975. [d] In addition to GC–MS.

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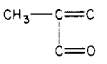
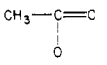
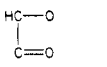
Table II. Summary of the Compounds Synthesized with Their Spectral Data

compd (mol wt)	mass spec major frag, %	proton NMR[a] assgnt	proton NMR[a] δ
6-methylguaiacol (138)	123 (100), 138 (99), 77 (20), 95 (14), 67 (11), 39 (11)	$ArCH_3$	2.27 (s, 3 H)
		OCH_3	3.87 (s, 3 H)
		ArOH	5.62 (br s, 1 H)
		ArH	6.72 (s, 3 H)
4-propylguaiacol (166)	137 (100), 166 (25), 138 (10), 122 (7), 94 (5), 52 (5)	CH_3	0.95 (t, 3 H)
		CH_2	1.61 (m, 2 H)
		$ArCH_2$	2.51 (t, 2 H)
		OCH_3	3.84 (s, 3 H)
		ArOH	5.5 (br s, 1 H)
		ArH	6.66 (br d, 1 H)
			6.82 (d, 1 H)
			6.69 (s, 1 H)
4-ethyl-2,6-dimethoxyphenol (182)	167 (100), 182 (60), 168 (20), 43 (15)	CH_3	1.24 (t, 3 H, J = 7 Hz)
		$ArCH_2$	2.6 (q, 2 H, J = 7 Hz)
		$ORCH_3$	3.85 (s, 6 H)
		ArOH	5.3 (br s, 1 H)
		ArH	6.4 (s, 2 H)
4-propyl-2,6-dimethoxyphenol (196)	167 (100), 196 (42), 168 (14), 41 (8), 53 (6)	CH_3	0.91 (t, 3 H)
		CH_2	1.61 (m, 2 H)
		$ArCH_2$	2.51 (t, 2 H)
		OCH_3	3.84 (s, 6 H)
		ArOH	5.4 (s, 1 H)
		ArH	6.4 (s, 2 H)
2,4,5-trimethyl-3(2*H*)-furanone (126)	54 (100), 126 (40), 43 (24), 39 (20), 55 (13), 53 (11)	CH_3	1.40 (d, 3 H, J = 9 Hz)
			1.65 (s, 3 H)
			2.15 (s, 3 H)
			4.35 (q, 1 H, J = 9 Hz)

[a] In $CDCl_3$; Me_4Si as internal standard; 100 MHz.

characteristic for bacon; acidic fraction, no aroma and taste.

Because the phenolic fraction was organoleptically evaluated as the most important contributor to the bacon flavor, it was selected to be analyzed. However, direct GC–MS analysis of this fraction did not reveal the identity of the minor components. Consequently, column chromatography was chosen to further separate the components for spectral analysis.

Column Chromatography. The phenolic fraction (0.4 g) was loaded onto a 10% deactivated SiO_2 column (14 g in 24 cm × 14 mm i.d.) and eluted with gradient solvents of isopentane, diethyl ether, and methanol, to yield eight subfractions. Evaluations of these eight subfractions are as follows [subfraction (150-mL each), character]: 1 (1% ether in isopentane), guaiacol, vanilla-baked goods, very pleasant; 2 (2% ether in isopentane), phenolic notes dominate, not very pleasant; 3 (4% ether in isopentane), phenolic, sour effect, leather note; 4 (7% ether in isopentane), fruity, nutty, walnut kernals; 5 (12% ether in isopentane), coconut, lactone; 6 (18% ether in isopentane), weak phenolic, sweet; 7 (ether), very weak odor; 8 (methanol), very weak, no odor.

Subfractions 7 and 8 were odorless and did not show any peaks by GC using FID detector. Therefore, these subfractions were not analyzed further.

Identification of Components. Subfractions of 1–6 were analyzed by gas chromatography–mass spectrometry (GC–MS) on a Carbowax 20M-TPA packed column (10 ft × $^1/_8$ in.). Identifications were confirmed by nuclear magnetic resonance (NMR) and/or by GC retention times (I_E values) from which the isolates were compared with either purchased or synthesized compounds.

Synthesis of Compounds. 4-Propylguaiacol and 4-propyl-2,6-dimethoxyphenol were prepared by hydrogenation of eugenol and 4-allyl-2,6-dimethoxyphenol, respectively, using palladium on activated carbon in methanol in a 500-mL Parr shaker.

6-methylguaiacol and 4-ethyl-2,6-dimethoxyphenol were prepared by Clemmensen reduction with amalgamated zinc and hydrochloric acid from 3-methoxysalicylaldehyde and 3′,5′-dimethoxy-4′-hydroxyacetophenone, respectively.

2,4,5-Trimethyl-3(2*H*)-furanone was prepared by aldol condensation of 2,3-pentanedione (Shu et al., 1980).

RESULTS

Table I lists the identification of 43 components constituting 95% of the total volatiles in the phenolic fraction of the cooked bacon. Table II shows the compounds synthesized for the structure confirmation along with their NMR and mass spectral data. Organoleptic evaluation of the components revealed that no single compound possessed the fried bacon odor, but rather that the fried bacon flavor may be due to a combination of various components. Of the individual components, 2,4,5-trimethyl-3(2*H*)-furanone is particularly noteworthy as it possesses an interesting caramel character in both aroma and taste.

It is of interest to notice the origins of the components identified from this study. The phenols, guaiacols, and the 2,6-dimethylphenols could be associated with the smoke used for the bacon process (Knowles et al., 1975). The lactones could be formed from the heating of pork fat (Watanabe and Sato, 1969). Cyclotene and its related compounds, which are the α-cyclodicarbonyls, may be generated from the sugar via Maillard reaction (Vernin and Parkanyi, 1982). As 2,4,5-trimethyl-3(2*H*)-furanone has been synthesized in this study from 2,3-pentanedione, which is also an α-dicarbonyl, this furanone may be also generated from sugar via Maillard reaction and aldol condensation (Shu et al., 1980; Piloty et al., 1979).

ACKNOWLEDGMENT

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Registry No. Phenol, 108-95-2; *o*-cresol, 95-48-7; *m*-cresol, 108-39-4; *p*-cresol, 106-44-5; 2-ethylphenol, 90-00-6; 4-ethylphenol, 123-07-9; 2,6-dimethylphenol, 576-26-1; ionol, 128-37-0; guaiacol, 90-05-1; 4-methylguaiacol, 93-51-6; 4-ethylguaiacol, 2785-89-9; 4-propylguaiacol, 2785-87-7; 4-isopropylguaiacol, 53587-16-9; 4-vinylguaiacol, 7786-61-0; eugenol, 97-53-0; *cis*-isoeugenol, 5912-86-7; *trans*-isoeugenol, 5932-68-3; 6-methylguaiacol, 2896-67-5; 6-ethylguaiacol, 90534-46-6; vanillin, 121-33-5; acetovanillone, 498-02-2; 2,6-dimethoxyphenol, 91-10-1; 4-methyl-2,6-dimethoxyphenol, 6638-05-7; 4-ethyl-2,6-dimethoxyphenol, 14059-92-8; 4-propyl-2,6-dimethoxyphenol, 6766-82-1; γ-valerolactone, 108-29-2; γ-hexalactone, 695-06-7; γ-nonalactone, 104-61-0; Δ-hexalactone, 823-22-3; Δ-heptalactone, 3301-90-4; Δ-octalactone, 698-76-0; Δ-nonalactone, 3301-94-8; 2,4-methyl-2-buteneolide, 5584-69-0; cyclotene, 80-71-7; 3,5-dimethylcyclopentane-1,2-dione, 13494-07-0; 3,4-dimethylcyclopentane-1,2-dione, 13494-06-9; 3-ethylcyclopentane-1,2-dione, 13494-08-1; acetic acid, 64-19-7; propionic acid, 79-09-4; octanoic acid, 124-07-2; decanoic acid, 334-48-5; 2-ethylhexanoic acid, 149-57-5; 2,4,5-trimethyl-3-(2*H*)-furanone, 64880-73-5.

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Functional and Physical Property Characterization of Peanut Milk Proteins Partially Hydrolyzed by Immobilized Papain in a Continuous Reactor

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A laboratory-scale reactor was designed in which immobilized papain was used to continuously hydrolyze peanut flour milk (PFM) at 52 °C and pH 7.2 for 10 h of operation time. The reaction volume was 150 mL, and the flow rate was 100 mL/h. Enzyme activity was maintained for 6 h under continuous purging with nitrogen and then decreased with time. A reduction in molecular weight of proteins in PFM was observed by subjecting samples to gel electrophoresis and gel filtration chromatography. The hydrolyzed peanut flour milk (HPFM) had improved nitrogen solubility at pH 4.5–7.0 and thermal stability at pH 5.0. The emulsion capacity of HPFM was slightly less than that of PFM. Freeze-dried HPFM incorporated (1%, w/v) into grape and apple juices resulted in nitrogen solubilities of 59.6 and 65.4%, respectively.

INTRODUCTION

Batch processes using papain to partially hydrolyze defatted peanut flour protein have been reported (Sekul and Ory, 1977; Sekul et al., 1978). In these studies, complete hydrolysis of peanut protein was observed in a 10% peanut flour slurry treated with a 0.5% aqueous solution of peptidase-free papain. Consequently, the formation of bitter peptides caused by excessive hydrolysis of protein did not occur. Hydrolysis had a desired effect in that protein functionality was modified, resulting in advantages when hydrolyzates were incorporated into certain foods. A similar batch process using bromelain to hydrolyze defatted peanut flour suspension followed by incorporation of hydrolyzates into cookie formulas has been studied (Beuchat et al., 1975; Beuchat, 1977a,b). Improvement of cookie-baking properties as well as fortification of wheat flour with high-protein peanut flour were achieved. These reports gave further encouragement to investigating the use of plant proteases (papain, bromelain, ficin) to modify vegetable protein for increased usage in the food industry. However, in batch processes, enzymes can be used only once, and most systems are energy and labor intensive.

A continuous system using a protease in an ultrafiltration reactor to modify soy protein isolates has been reported (Deeslie and Cheryan, 1981). In a previous study in our laboratory, immobilization of papain on an anion-exchange resin (Dowex MWA-1, 20–50 mesh) was achieved with considerable success. In that study, both immobilized papain and soluble papain were labile to air, which indicated that oxygen inactivation of immobilized papain through formation of disulfide bonds with sulfhydral groups of papain is a hindrance for application in a continuous system. However, in a long-term storage test, the activity of immobilized papain could be satisfactorily maintained by depletion of oxygen in a closed system followed by nitrogen purging. Theoretically, in a continuous system, depletion of oxygen could be obtained by a similar procedure. A laboratory-scale continuous reactor was therefore designed so that immobilized papain activity

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