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Characterization of Nonbasic Steam Volatile Components of Potato Chips

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The nonbasic fraction of the steam volatile oil from potato chips has been analyzed using capillary and packed column gas chromatography separation, with characterization by mass and infrared spectrometry. Forty-six compounds were characterized,

of which 25 had not been previously reported in potato chips. In the authors' opinion some of the more important aroma compounds in this fraction include methional, 3-methylbutanal, phenylacetaldehyde, and deca-*trans*-2,*trans*-4-dienal.

A number of volatile nonbasic components of potato chips have been characterized previously by Chang (1967) and Mookerjee *et al.* (1965). The present work was begun with the belief that a comprehensive knowledge of the compounds responsible for the desirable flavor of potato chips could help the development of low fat fried potato products which are more desirable from a nutritional standpoint. The authors previously reported characterization of volatile basic components of potato chips (Buttery *et al.*, 1971).

EXPERIMENTAL

Materials. For the major part of the work using direct capillary gas-liquid chromatography (glc) mass spectral analysis, good quality potato chips were obtained from local retail markets. To obtain larger quantities of steam volatile oil for confirmatory work by infrared absorption (ir) spectrometry, so-called "cull" potato chips were obtained from a local manufacturer. These were generally of reasonable color and flavor but were screened out by the manufacturer because they consisted mainly of small broken pieces. Both "cull" and good quality potato chips, of the same brand, gave steam volatile oils with essentially the same glc pattern.

Many authentic samples of organic compounds were obtained from reliable commercial sources. In addition, a considerable number were synthesized by well established procedures. For example, 2,4-dienals were synthesized by the procedure of Pippen and Nonaka (1958); alkylfurans were synthesized by the method of Gilman and Calloway (1933). 5-Methylhex-*trans*-2-enal was synthesized by condensation of 3-methylbutanal with malonic acid in pyridine to give 5-methylhex-2-enoic acid. This acid was converted to its methyl ester. The ester was reduced with LiAlH_4 to give 5-methylhex-2-enol. This alcohol was oxidized with MnO_2

to give 5-methylhex-2-enal. This compound had been previously synthesized by Jutz (1958).

Isolation of Steam Volatile Oil and Separation into Basic and Nonbasic Fractions. The steam volatile oil was obtained and separated into its basic and nonbasic fractions as described previously (Buttery *et al.*, 1971).

Capillary glc Mass Spectral Analysis. The method used is essentially the same as that described previously by the authors (Buttery *et al.*, 1969) except that helium was used as the carrier gas and that three different studies were made using different columns. The columns were a 1000-ft \times 0.03-in. i.d. stainless steel capillary coated with Silicone SF 96-100 containing 5% Igepal CO-880; a 1000-ft \times 0.03-in. i.d. stainless steel capillary coated with Carbowax 4000 containing 5% Igepal CO-880; and a 500-ft \times 0.03-in. i.d. stainless steel capillary coated with diethyleneglycolsuccinate polyester (DEGS). The silicone column was programmed from 50 to 170°C at 1/2°C per min and held. The Carbowax column was programmed from 60 to 170°C at 1/2°C per min and held. The DEGS column was programmed from 25 to 70°C at 1°C per min and then from 70 to 150°C at 1/2°C per min. Injector temperature was 170-200°C.

Separation of Samples for Infrared (ir) Spectra. This was carried out using packed column glc similar to that described previously (Buttery *et al.*, 1969). Infrared spectra were recorded with a Perkin-Elmer 237 instrument using carbon tetrachloride solutions in ultramicro cavity cells and a reflecting beam condenser.

RESULTS AND DISCUSSION

The steam volatile oil, from fresh good potato chips, was isolated and separated into basic and nonbasic fractions as described previously by the authors (Buttery *et al.*, 1971). It was then analyzed by the combination of capillary glc and mass spectrometry, as outlined in the experimental section. Table I lists components characterized in the nonbasic fraction. Approximate relative percentages of components in the

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isolated steam volatile oil are also listed. These were obtained using glc peak areas. There is considerable variation with different batches of the same brand of chips, and these figures are only meant to give a general idea of the relative amounts. Packed column glc resolution of the components of the nonbasic fraction from "cull" potato chips provided sufficient material for the infrared spectral verification shown in Table I.

Most of the straight chain aldehydes and ketones, listed in Table I, had been previously characterized by Chang and co-workers (Chang, 1967; Mookerjee *et al.*, 1965). These most likely arise from the vegetable oil used in the cooking. A few had not previously been characterized. One of the most interesting of these is an apparent decatrienal for which the authors obtained good mass spectral and ir spectral information, but were unable to characterize it as any known compound. The mass spectrum (two major ions each 14 units above m/e 28, intensities in parentheses) showed a molecular ion at m/e 150 (33), important ions at: 39 (74), 41 (62); 43 (42), 55 (42); 65 (34), 69 (20); 77 (100), 79 (35); 91 (71), 94 (75); 103 (17), 107 (17); 121 (100); and 135 (5). The ir spectrum showed many similarities to that of deca-*trans*-2, *trans*-4-dienal with absorption at 3.7 μ characteristic of an aldehyde and at 6.0 and 6.2 μ characteristic of a 2,4-dienal. Deca-*trans*-2, *trans*-4, *trans*-6-trienal was synthesized by condensing hex-2-enal with the Grignard reagent from 1-methoxybut-1-en-3-yne followed by LiAlH_4 reduction and hydrolysis following the 2,4-dienal synthesis procedure of Pippen and Nonaka (1958). Its infrared and mass spectra were, however, quite different from those of our unknown. The next most likely structure is deca-*trans*-2, *trans*-4, *cis*-7-trienal, as this would be an understandable breakdown product from linolenic acid. This structure is reasonably consistent with the infrared and mass spectra; however, no authentic sample was available for comparison.

5-Methylhex-*trans*-2-enal is somewhat unusual. It is possibly formed in the potato chips from the condensation of 3-methylbutanal and acetaldehyde (or precursor) during the normal high cooking temperatures. Its mass spectrum showed a molecular ion at 112 (3) and other important ions at: 39 (55), 41 (100), 43 (83), 55 (29); 69 (35), 70 (100); 81(4), 83 (17); and 94 (13), 97 (14).

The alkylfurans listed in Table I also possibly originate from the oil, as Chang *et al.* (1966) have found pentylfuran in vegetable oil. This may not necessarily be the origin, however, because the authors (Buttery *et al.*, 1970) found pentylfuran as a major product in the volatile oil from atmospheric steam distilled potatoes. Alkylfurans have also been found in cooked chicken volatiles (Nonaka *et al.*, 1967) and other heated products (Stoll *et al.*, 1967).

The more oxygenated furans such as 2-acetylfuran and 5-methylfurfural fairly certainly arise from sugar or polysaccharide thermal degradation of the type studied by Hodge (1967). It is also probably true that other known sugar thermal degradation products such as 4-hydroxy-2,5-dimethyl-3-(2*H*)-furanone and 2-hydroxy-3-methyl-2-cyclopenten-1-one (Hodge *et al.*, 1972; Hodge, 1967) and related compounds must be present in the potato chips at some level of concentration. Unfortunately we were unable to detect these compounds. It is probable that the isolation methods used for the major part of this study are not applicable to small concentrations of such highly polar water-soluble materials. However, when fresh potato chips were ground in a mortar and eluted with pentane and dichloromethane in a glass chromatography column, the remaining chips still possessed a characteristic sweet burnt-like potato chip aroma. This aroma could be

Table I. Compounds Characterized in the Nonbasic Fraction of Potato Chips

Aliphatic compounds	Compounds ^{a, b}	Approx relative % in whole volatile oil	
Alkanals	2-Methylpropanal MS, RT	0.5	
	2-Methylbutanal MS, RT	7.4	
	3-Methylbutanal MS, RT	5.0	
	Pentanal ^c MS, RT	0.2	
	Hexanal ^c MS, IR, RT	2.1	
	Heptanal ^c MS, RT	0.6	
	Octanal ^c MS, RT	0.1	
	Nonanal ^c MS, RT	0.1	
	Alkenals	Hex- <i>trans</i> -2-enal ^c MS, IR, RT	0.2
		Hept- <i>trans</i> -2-enal ^c MS, IR, RT	1.8
Oct- <i>trans</i> -2-enal ^c MS, IR, RT		0.7	
Non- <i>trans</i> -2-enal ^c MS, IR, RT		1.5	
Dec- <i>trans</i> -2-enal ^c MS, IR, RT		1.2	
Undec- <i>trans</i> -2-enal ^c MS, RT		0.7	
5-Methylhex- <i>trans</i> -2-enal MS, IR, RT		0.8	
Alkadienals		Nona- <i>trans</i> -2, <i>cis</i> -4, -dienal MS, RT	t ^d
	Nona- <i>trans</i> -2, <i>trans</i> -4-dienal MS, RT	0.2	
	Deca- <i>trans</i> -2, <i>cis</i> -4-dienal MS, IR, RT	1.0	
	Deca- <i>trans</i> -2, <i>trans</i> -4-dienal ^e MS, IR, RT	7.5	
	Undeca- <i>trans</i> -2, <i>trans</i> -4-dienal MS, RT	t	
Ketones	Butan-2-one ^c MS, RT	t	
	Heptan-2-one ^c MS, RT	0.2	
	Octan-2-one ^c MS, RT	t	
	Decan-2-one ^c MS, RT	0.2	
	Butane-2,3-dione MS, RT	t	
	Pentane-2,3-dione MS, IR, RT	0.2	
	Pent- <i>trans</i> -3-en-2-one MS, RT	t	
	Non- <i>trans</i> -2-en-4-one MS, RT	t	
Alkanols	Pentanol IR, RT	0.3	
	3-Methylbutanol MS, RT	t	
	Butan-2-ol MS, RT	0.1	
Sulfur compounds	2-Methylmercaptoacetaldehyde MS, RT	0.1	
	3-Methylmercaptopropanal (methional) ^e MS, RT	2.0	
Hydrocarbons	1-Decyne ^c MS, RT	1.6	
Aromatic compounds			
Aldehydes	Benzaldehyde ^c MS, RT	2.2	
	Phenylacetaldehyde ^c MS, RT	18	
Oxygen heterocyclics	2-Butylfuran MS, RT	0.1	
	2-Pentylfuran MS, RT	0.1	
	2-Hexylfuran MS, RT	t	
	Furfural ^c MS, RT	0.8	
	2-Furfuryl alcohol, MS, RT	0.1	
	2-Acetylfuran ^b MS, RT	0.5	
	5-Methylfurfural MS, RT	t	
Nitrogen heterocyclics	2-Methyl-3-ketotetrahydrofuran MS, IR, RT	0.3	
	2-Acetylpyrrole MS, IR, RT	0.6	
Terpenoids			
Alcohols	α -Terpineol MS, RT	0.3	

^a MS, IR, RT—mass spectral, infrared spectral, and glc evidence, respectively. ^b Evidence cited under this column is consistent with that of an authentic sample obtained on the same instrument. ^c Previously reported in potato chips (Chang, 1967; Mookerjee *et al.*, 1965). ^d t Means less than 0.1%. ^e Previously found by Chang (1971).

eluted with methanol. Removal of the methanol by distillation gave a residue with this characteristic aroma. The compound or compounds mainly responsible for this aroma were apparently unstable, however, as the isolated aroma fraction lost its characteristic aroma on storage at -20°C overnight or in a few hours at room temperature. Several attempts have

been made to isolate the compound or compounds responsible for this aroma but without success. A special approach will be necessary to fit the high polarity of this compound(s) and its unstable nature.

Importance of the Components to the Aroma of Potato Chips.

The authors are in the process of measuring odor thresholds and carrying out qualitative odor studies of the components of potato chips. The results of these studies will be reported when all the information is collected and analyzed. From results obtained so far, it is clear that the aroma of potato chips is a complex mixture. However, the authors believe that some of the more important compounds in the nonbasic fraction include 3-methylmercaptopropanal (methional), 3-methylbutanal, phenylacetaldehyde, and deca-*trans*-2,*trans*-4-dienal.

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Comparison of Carbonyl Compounds in Raw and Roasted Runner Peanuts. I. Major Qualitative and Some Quantitative Differences

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Carbonyl compounds present in oil cold-pressed from raw and roasted peanuts were converted into 2,4-dinitrophenylhydrazones and were identified by comparison of their R_f values, colors, uv, visible, and mass spectra with authentic compounds. Compounds in roasted peanuts included 14 aldehydes, 10 methyl ketones, nine 2-enals, and seven 2,4-dienals. Raw peanuts contained 10 aldehydes, eight methyl ketones, seven 2-enals, and four 2,4-dienals. Hexanal, octanal, nonanal, decanal, and pentanal were the major carbonyl compounds in

raw peanuts. Roasted peanuts contained very large concentrations of 2-methylpropanal, 2-methylbutanal, and 3-methylbutanal and large concentrations of 2-heptenal, 2-octenal, 2-nonenal, 2,4-decadienal, hexanal, octanal, and decanal. The average total carbonyl content and the carbonyl content of the dicarbonyl, ketoglyceride, and monocarbonyl fractions in raw peanuts were 62, 30, 24, and 8 μmol per 100 g of oil and in roasted peanuts were 324, 198, 99, and 26 μmol per 100 g of oil, respectively.

The presence of aldehydes and ketones in the aroma and flavor fraction from raw and roasted peanuts has been recognized for several years (Pattee *et al.*, 1965; Young and Holley, 1965; Mason *et al.*, 1967). Significant roles in the overall flavor and aroma of raw and roasted peanuts have been suggested for a few of these carbonyl compounds.

Pattee *et al.* (1965) identified 11 volatile compounds, including nine aldehydes and ketones, in high-temperature-cured, off-flavored peanuts. More recently Pattee *et al.* (1970) related the production of eight compounds, including four carbonyl compounds, to enzyme activities in maturing peanuts, and Pattee *et al.* (1969) strongly implicated hexanal with the characteristic aroma of raw peanuts. Several other sat-

urated aldehydes and 2-nonenal are reported to convey a beany flavor to oxidized milk fat (Kinsella, 1969) and could conceivably impart a beany flavor to raw peanuts too.

The change to a highly desirable roasted peanut flavor that occurs during roasting is ascribed to pyrolytic reactions between amino acids and reducing sugars (Mason *et al.*, 1969) and to the volatile carbonyl compounds (Young and Holley, 1965) and pyrazines (Mason *et al.*, 1966) which are thus produced. More recently Mason *et al.* (1967) positively identified ethanal, 3-methylbutanal, benzaldehyde, and phenylacetaldehyde and tentatively identified four other aldehydes and ketones in condensates from roasted Spanish peanuts. These authors also noted that if the low molecular weight aldehydes were removed from the condensate, the harsh aroma associated with freshly roasted peanuts was no longer present. Ball-schmieter and Germishuizen (1968) correlated the production of 2-methylpropanal with the development of roasted peanut flavor but did not find evidence for the presence of

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