Characterization of Volatile Pyrazine and Pyridine Components of Potato Chips

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The basic 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 spectrometries. The identities of 18 pyrazine and pyridine compounds were confirmed by comparison of their spectral data with those of authentic compounds or with published spectra. Tentative identities were obtained for an additional eight alkylpyrazines from their mass spectral fragmentation patterns. Informal sensory evaluation indicated that 2-ethyl-3,6-dimethylpyrazine, a major component of the oil, was one of the most potent odorants isolated and is probably a major contributor to the odor intensity of the basic fraction.

Considerable work on the characterization of the nitrogen containing flavor components of potato chips has been carried out by Chang and coworkers (Deck and Chang, 1965; Chang, 1967) who reported the characterization of seven pyrazine components and pyridine.

A large portion of the annual potato crop is processed into some kind of fried form, notably potato chips and french fries. The popularity of such items is generally associated with their unique and desirable flavor. Unfortunately these fried products have high oil contents which restrict their use for an increasingly large number of consumers on low-fat diets. French fries and potato chips can be produced, at least on a pilot plant scale, with considerably less oil (Weaver and Huxsoll, 1970) but they lack the desirable flavor of the normal high oil content product. This work was undertaken with the aim of learning more about fried potato flavor to provide a basis for the development of methods of enhancing the fried flavor of such low-fat potato products.

The formation of pyrazines is one of the major changes that take place during the cooking of potato chips. The present study was directed at the characterization of the pyrazine and other basic components with the hope of obtaining a more comprehensive picture of their role in fried potato flavor.

EXPERIMENTAL

Materials. For the major part of the work using direct capillary gas chromatography mass spectral analysis, good quality potato chips were obtained from local retail markets. To obtain larger quantities of oil, for confirmatory work by infrared absorption spectra, 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 gas–liquid chromatography (glc) pattern.

Authentic samples of pyrazines were generally synthesized by procedures already described in the literature (Flament *et al.*, 1967). 2-Acetylpyridine was synthesized in about 10% yield by heating an intimate mixture of calcium acetate and calcium α-picolinate to 425° C (Engler and Rosumoff, 1891).

Isolation of Steam Volatile Oil. The method used to isolate the steam volatile oil from potato chips is similar to that described previously by the authors for other products such as carrots, etc. (Buttery *et al.*, 1968) using a Likens–Nickerson steam distillation continuous extraction head (Nickerson and Likens, 1966).

The isolation was conducted under vacuum and at atmospheric pressure using diethyl ether as solvent but essentially the same glc pattern was obtained from both methods (for pyrazine components), and therefore atmospheric pressure was used for the major part of the work. The freshly distilled ether used for extraction and the extracted oil were protected against oxidation by the addition of a trace (less than 1% of the extracted oil) of the essentially nonvolatile antioxidant Ionox-330.

For good quality retail size potato chips a laboratory scale apparatus was used for the steam distillation continuous extraction. Each charge consisted of 1500 g of potato chips and 8 l. of odor free distilled water in a 12-l. flask with 100 ml of diethyl ether in the solvent side arm flask. For cull potato chips a 90-l. glass-lined steam jacketed container was used with a proportionately scaled up Likens–Nickerson steam distillation continuous extraction head. This apparatus held a charge of 17 kg of cull potato chips and 70 l. of water with 150 ml of diethyl ether in the solvent side arm flask. The steam distillation continuous extraction was usually carried out for 3 hr. The ether extract was dried over a small quantity of sodium sulfate, and the ether was removed through low holdup distillation columns to give the potato chip oil (10–30 ppm of the chips).

Isolation of the Basic Fraction. Approximately 0.1 g of potato chip steam volatile oil was taken up in freshly distilled diethyl ether (100 ml) and extracted with 3 *N* hydrochloric acid (3 × 50 ml). After further extraction with ether (50 ml) to remove traces of nonbasic components, the combined aqueous acid extract was neutralized with excess sodium bicarbonate and the liberated basic compounds extracted with ether (4 × 40 ml). The ether extract was dried over a small quantity of sodium sulfate and the ether was removed using low holdup distillation columns to give the basic fraction (*ca.* 0.02 g).

Capillary Glc Mass Spectral Analysis. The method used is essentially the same as that described in a previous publication by the authors (Buttery *et al.*, 1969) except that helium was used as the carrier gas.

Separation of Samples for Infrared (ir) Spectra. This was also 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.

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Table I. Identities of Constituents of Basic Fraction of the Steam Volatile Oil of Potato Chips

Confirmed identity[a,b]	Predicted tentative identity	Approximate relative amount[c]
Pyridine[d] (ms, ir, RT)		s
2-Methylpyrazine (ms, ir, RT)		m
2,5-Dimethylpyrazine[d] (ms, ir, RT)		l
2,6-Dimethylpyrazine[d] (ms, RT)		m
2,3-Dimethylpyrazine (ms, RT)		m
2-Ethylpyrazine[d] (ms, RT)		m
2-Ethyl-5-methylpyrazine[d] (ms, ir, RT)		l
2-Ethyl-6-methylpyrazine (ms, ir, RT)		m
2-Ethyl-3-methylpyrazine (ms, RT)		m
2,3,5-Trimethylpyrazine[d,e]		s
2-Methyl-5-vinylpyrazine[e] (ms, ir)		s
	2-Methyl-6-vinylpyrazine (ms)	s
2-Acetylpyridine (ms, ir, RT)		s
2-Ethyl-3,6-dimethylpyrazine[d] (ms, ir, RT)		l
2-Ethyl-3,5-dimethylpyrazine[e] (ms)		m
2,6-Diethylpyrazine (ms, RT)		m
	2,5-Dimethyl-3-vinylpyrazine (ms)	s
2-Isobutyl-3-methylpyrazine (ms, RT)		s
2,3-Diethyl-5-methylpyrazine[e] (ms)		m
	2,5-Dimethyl-6-isopropylpyrazine (ms)	s
2-Isobutyl-3,6-dimethylpyrazine (ms, ir, RT)		m
	2-Isoamyl-5-methylpyrazine (ms)	s
	Methylethylisobutylpyrazine (ms)	s
	2-Isobutenyl-3-methylpyrazine (ms)	s
	2-Isoamyl-3,6-dimethylpyrazine (ms)	s
	Isobutenyldimethylpyrazine (ms)	s

[a] ms, ir, RT = mass spectral, infrared absorption, and glc retention evidence, respectively. [b] Evidence cited under this column is consistent with that of an authentic sample obtained on the same instrument unless otherwise indicated (see e below). [c] l = relatively large, m = moderate, and s = small. [d] Previously reported in potato chips (Deck and Chang, 1965; Chang, 1967). [e] No authentic sample available but spectra consistent with published spectra (Bondarovich, 1967).

RESULTS AND DISCUSSION

Table I lists components characterized in the basic fraction using capillary glc mass spectral analysis. Capillary glc mass spectral analysis was also carried out on the whole steam volatile potato chip oil to verify that no artifacts were formed by the acid extraction. Packed column glc separation of components from the cull potato chip basic fraction provided material for the infrared spectral verification shown in Table I.

The mass spectra of most compounds in Table I have been reported by Bondarovich *et al.* (1967). Mass spectra obtained in the present work of both synthetic and found compounds were consistent with these. The mass spectra found for lesser known compounds are listed below (above *m/e* 40, intensities in parentheses with the base peak taken as 100): 2-isobutyl-3-methylpyrazine, mol ion 150 (5), major ions 108 (100), 41 (17), 42 (13), 67 (12), 135 (10), 43 (9), 53 (5), 93 (4), 94 (3), 60 (1), 82 (1); 2-isobutyl-3,6-dimethylpyrazine, mol ion 164 (6), major ions 122 (100), 42 (36), 41 (17), 53 (12), 149 (10), 43 (10), 108 (8), 80 (4), 67 (3); 2-acetylpyridine, mol ion 121 (43), major ions 79 (100), 43 (77), 78 (76), 52 (42), 51 (35), 93 (15), 50 (15), 42 (12), 106 (4), 94 (3), 108 (2), 66 (2).

With tentatively characterized compounds the major important ions found (with molecular ions in heavy type) were as follows: 2-methyl-6-vinylpyrazine **120**, 52, 54, 119, 94, 42, 79; 2,5-dimethyl-3-vinylpyrazine 133, **134**, 42, 54, 91, 66, 108; 2,5-dimethyl-6-isopropylpyrazine 122, **150**, 149, 135, 42, 53, 67; 2-isoamyl-5-methylpyrazine 108, 122, 42, 149, 67, 53, **164**; methylethylisobutylpyrazine 136, 121, 108, 53, 163, **178**; 2-isobutenyl-3-methylpyrazine **148**, 119, 133, 52, 55, 66, 67; 2-isoamyl-3,6-dimethylpyrazine 122, 42, 53, 135, 163, 80, **178**; isobutenyldimethylpyrazine **162**, 133, 147, 79, 52, 108, 121.

Eight of the compounds listed in Table I had previously been reported in potato chips by Chang and coworkers (Deck and Chang, 1965; Chang, 1967). A number have also recently been reported (Sapers *et al.*, 1970) in explosion puffed dehydrated potato. Many of the other pyrazines have been reported in other roasted products, including coffee (Goldman *et al.*, 1967), chocolate (Marion *et al.*, 1967) and roasted peanuts (Mason *et al.*, 1966; Walradt *et al.*, 1970; Johnson and Waller, 1970). A major important pyrazine in potato chips is 2-ethyl-3,6-dimethylpyrazine. Koehler *et al.* (1969) have shown that in model systems the glutamic acid–glucose reaction produces a large amount of 2-ethyl-3,6-dimethylpyrazine. It is notable that glutamic acid occurs in appreciable amounts in potatoes (Talley *et al.*, 1970).

Aroma Significance of Pyrazine and Pyridine Components. Informal sensory evaluation by four experienced persons indicated that the diluted freshly extracted steam volatile potato chip oil had an odor moderately similar to that of the original potato chips. Furthermore the basic fraction obtained from this oil by extraction with dilute hydrochloric acid was considered to have an aroma resembling that of potato chips. Thus it is reasonable to expect that at least some of the components isolated from the basic fraction make important contributions to the aroma of fresh potato chips. Preliminary sensory evaluation indicated that 2-ethyl-3,6-dimethylpyrazine is one of the most potent odorants derived from chips, and that in low concentrations it could make a definite contribution to potato chip aroma. Although 2-acetylpyridine was characterized as having a cracker type aroma, this and many related compounds could be important to the total potato chip odor. It is possible that the compound (in chips) mainly responsible for the cracker aroma contribution is 2-acetyl-1,4,5,6-tetrahydropyridine (Hunter *et al.*, 1969). This compound is a very potent odorant, but during the isolation it may be changed to the more stable 2-acetylpyridine and other products. Pure synthetic 2-acetyl-1,4,5,6-tetrahydropyridine decomposes on storage, even at low temperatures, giving a number of products. One of the major products of this decomposition has been characterized as 2-acetylpyridine (Buttery, 1970).

As is usually the case, there does not appear to be one or two compounds which can be considered as largely responsible for the desirable aroma of fresh potato chips. However, a number of the isolated compounds appear to have the potential as contributors to chip aroma. Detailed sensory evaluation of these compounds, including thresholds and descriptive odor analysis, is underway and will be the subject of a future report.

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