

genic activity. It is necessary to study further to determine their structures and the correlations between them and the mutagens in browning reaction systems.

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#### LITERATURE CITED

- Ames, B. N., Durston, E. W., Yamasaki, E., Lee, F. D., *Proc. Natl. Acad. Sci. U.S.A.* **70**, 2281 (1973).
- Ames, B. N., NcCann, J., Yamasaki, E., *Mutat. Res.* **31**, 347 (1975).
- Bonner, W. A., zu Reckendor, W. N., *Chem. Ber.* **94**, 225 (1961).
- Druckery, G., Preussmann, R., Ivankovic, S., Schmägl, D., *Z. Krebsforsch.* **69**, 103 (1967).
- Freund, G. A., *Ann. Internal. Med.* **10**, 1144 (1937).
- Hodge, J. E., *Cereal Sci. Today* **17**, 34 (1972).
- Kitamura, K., Sakaguchi, M., Okamoto, Y., Shibamoto, T., "Study of non-Volatile Constituents Produced from the Reaction of D-Glucose and Cysteamine", Fifth International Congress of Food Science and Technology, Kyoto, 1978, Abstract No. 5d-17.
- Lijinsky, W., Epstein, S. S., *Nature (London)* **225**, 21 (1970).
- Maga, J. A., *Crit. Rev. Food Sci. Nutr.* **6**, 153 (1975).
- Magee, P. N., Barnes, J. M., *Br. J. Cancer* **10**, 114 (1956).
- Nagao, M., Yahagi, T., Sugimura, T., Ito, N., *Mutat. Res.* **42**, 335 (1977).
- Newell, J. A., Mason, M. E., Matlook, R. S., *J. Agric. Food Chem.* **15**, 767 (1967).
- Ray, S., *J. Chromatogr.* **153**, 173 (1978).
- Sakaguchi, M., Shibamoto, T., *J. Agric. Food Chem.* **26**, 1179 (1978).
- Sakaguchi, M., Shibamoto, T., *Agric. Biol. Chem.* **43**, 667 (1979).
- Sugimura, T., Sato, S., Nagao, M., Yahagi, T., Matsushima, T., Seino, Y., Takeuchi, M., Kawachi, T., "Fundamentals in Cancer Prevention", University of Tokyo Press/University of Pank Press, Baltimore, MD, 1976, p 191.
- Tondeur, R., Sion, R., Deray, E., *Bull. Soc. Chim. Fr.*, 2493 (1964).
- Yamaguchi, K., Sakakibara, S., Asamizu, J., Ueda, I., *Biochim. Biophys. Acta* **297**, 48 (1973).
- Zeiger, E., Sheldon, A. T., *Mutat. Res.* **57**, 1 (1978).

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## Chemistry of Baked Potato Flavor. 1. Pyrazines and Thiazoles Identified in the Volatile Flavor of Baked Potato

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The volatile flavor was isolated from 540 lb of Idaho Russet Burbank baked potatoes. Extensive gas chromatographic analysis yielded 420 fractions. The odor of each chromatographic fraction was evaluated, and the fractions were identified by infrared and mass spectrometry. Thirty-one pyrazines and three thiazoles were identified. The results of this work indicate that a natural baked potato flavor is not due to a single compound, but is the result of the mixture of a number of components.

Of all the forms of cooked potato, the flavor produced by baking potatoes is perhaps the most interesting because of its weak but distinct quality.

Baked potatoes are unique because they are cooked as is, only in air at high temperatures without the use of cooking oil, which has been shown to play a vital part in flavor development (Deck et al., 1973). Therefore, the volatile flavor of baked potatoes originates from the potato not from an interaction between the oil and the food, or from the oil. Also, a potato with a higher solids content is used for baking and the outer layer and skin of the potato are retained during preparation. These unique features of the potatoes used and the method employed for preparing baked potatoes play a significant role in the development of the very mild but distinct flavor.

With the identification of 2,5-dimethylpyrazine in the volatiles of potato chips (Deck and Chang, 1965) and roast peanuts (Mason, et al. 1966), pyrazines were uncovered as an extremely important class of flavor compounds in potatoes and other foods (Maga and Sizer, 1973a, b). Pyrazines have also been reported in the volatile flavor of baked potato. Buttery et al. (1973a, b) reported the identification of 45 compounds, mostly pyrazines and aliphatic aldehydes, as volatile flavor components of Washington Russet Burbank potatoes. The authors consider the following compounds to be the most important

to baked potato aroma: 2-ethyl-3,6-dimethylpyrazine, methional, deca-*trans,trans*-2,4-dienal, and possibly, 2-ethyl-3,5-dimethylpyrazine. In the most recent report, Pareles and Chang (1974) identified 16 compounds in baked potato flavor. Among the compounds identified it was believed that a combination of 2-isobutyl-3-methylpyrazine, 2,3-diethyl-5-methylpyrazine, and 3,5-diethyl-2-methylpyrazine had an odor closer in character to baked potato aroma than did any single compound.

Baked potato flavor has not been extensively studied because of the difficulties involved in obtaining a natural flavor isolate collected from the headspace of baked potatoes in sufficient concentration for chemical analysis. The present paper reports on the identification of pyrazine and thiazole compounds isolated and fractionated from a genuine baked potato flavor.

#### EXPERIMENTAL SECTION

**Isolation of the Volatile Flavor.** The volatile flavor was isolated from Idaho Russet Burbank potatoes (with skins) baked at 205 °C for 105 min, the apparatus previously described by Chang et al. (1977). The principle of the apparatus is removal and subsequent condensation of the volatile flavor in the headspace of the baked potatoes. The flavor was not isolated from a water slurry of baked potatoes but from the food as it exists under normal conditions. Thirty pounds of baked potatoes was used for each isolation which lasted 48 h. After 48 h there was a definite decrease in the quality of the flavor in the headspace of the baked potatoes. Due to the low concentration of the flavor in the headspace of the food and

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Table I. Pyrazines and Thiazoles Identified in the Volatile Flavor of Baked Potato<sup>a</sup>

	first reported in baked potato	first reported in potato	mass spectral identification	infrared spectral identification	mass spectra reference
thiazoles					
2,5-dimethyl-4-ethylthiazole	+	+	+	-	Buttery et al. (1973b)
2,5-dimethyl-4-butylthiazole*	+	+	+	-	Buttery et al. (1973b)
2,5-diethyl-4-methylthiazole*	+	+	+	-	Buttery et al. (1973b)
pyrazines					
methylpyrazine	-	-	+	+	Kinlin et al. (1972)
2,3-dimethylpyrazine	-	-	+	+	Kinlin et al. (1972)
2,5-dimethylpyrazine	-	-	+	+	Kinlin et al. (1972)
2,6-dimethylpyrazine	-	-	+	+	Kinlin et al. (1972)
ethylpyrazine	-	-	+	+	Bondorovich et al. (1967)
2-ethyl-3-methylpyrazine*	-	-	+	+	Kinlin et al. (1972)
2-ethyl-5-methylpyrazine	-	-	+	+	Kinlin et al. (1972)
2-ethyl-6-methylpyrazine	-	-	+	+	Kinlin et al. (1972)
2,3,5-trimethylpyrazine	-	-	+	+	Kinlin et al. (1972)
2,3-diethylpyrazine	+	+	+	+	Kinlin et al. (1972)
2-ethyl-3,6-dimethylpyrazine*	-	-	+	+	Kinlin et al. (1972)
2-ethyl-3,5-dimethylpyrazine*	+	+	+	+	Friedel et al. (1971)
2-ethyl-6-vinylpyrazine*	+	+	+	+	Friedel et al. (1971)
2-butyl-3-methylpyrazine	+	+	+	-	Friedel et al. (1971)
2-butyl-6-methylpyrazine	+	+	+	+	108 (100%), 43 (11%), 39 (10.3%); 41 (9.2%), 58 (9.1%); 109 (7.7%)
2-isobutyl-3-methylpyrazine*	-	-	+	+	Buttery et al. (1971)
2,3-diethyl-5-methylpyrazine*	-	-	+	+	Kinlin et al. (1972)
3,5-diethyl-2-methylpyrazine*	-	-	+	+	Bondorovich et al. (1967)
2-ethyl-6-propylpyrazine	+	+	+	+	Friedel et al. (1971)
2-ethyl-3,5,6-trimethylpyrazine*	+	+	+	-	Friedel et al. (1971)
2,3-dimethyl-5-butylpyrazine*	+	+	+	-	Maga et al. (1973)
2,5-dimethyl-3-butylpyrazine*	+	+	+	+	Maga et al. (1973)
2,6-dimethyl-3-butylpyrazine*	+	+	+	-	Maga et al. (1973)
2,5-dimethyl-3-isobutylpyrazine*	+	+	+	-	Friedel et al. (1971)
3-isoamyl-2,5-dimethylpyrazine*	+	+	+	-	Friedel et al. (1971)
2-isopropyl-3-methoxy pyrazine	+	+	+	+	Seifert et al. (1970)
2-methyl-6,7-dihydro-5H-cyclopentapyrazine*	+	+	+	+	Pittet et al. (1974)
5-methyl-6,7-dihydro-5H-cyclopentapyrazine*	+	+	+	-	Kinlin et al. (1972)
3,5-dimethyl-6,7-dihydro-5H-cyclopentapyrazine*	+	+	+	+	Pittet et al. (1974)
5,7-dimethyl-1,2,3,4,7,8-hexahydroquinoxaline*	+	+	+	-	Kinlin et al. (1972)
2,3,6-trimethyl-5-hydroxycyclopentapyrazine	+	+	+	-	Pittet et al. (1974)
					136 (100%), 135 (46%), 178 (24.7%), 163 (18.6%), 137 (11.8%), 121 (11.4%)

<sup>a</sup> Asterisks indicate key component.

the very mild quality of the baked potato flavor, it became necessary to run 18 isolations. Therefore, the isolate contained the volatile flavor from 540 lb of baked potatoes. The total flavor isolate collected in the traps cooled in dry ice and acetone was treated in a manner similar to that described by Herz and Chang (1966). The aqueous layer of the flavor isolate was saturated with NaCl, extracted with anhydrous ethyl ether and recombined with the total flavor isolate. The baked potato flavor isolate (9000 mL) was dried with anhydrous sodium sulfate and then concentrated down to final volume of 3 mL with the use of a 30-plate Oldershaw column and a 200-plate spinning band still.

**Fractionation of the Flavor Isolate.** The initial preparative chromatography of the baked potato flavor isolate was performed on a Beckman GC-55 gas chromatograph equipped with a flame ionization detector, fitted with a 1/8 in. o.d. × 12 ft stainless steel column, packed with 10% OV-101 on 80/100 mesh Chromosorb W. The flow rate was 30 mL/min with a column temperature which was programmed from 40 to 250 °C at a rate of 2.5 °C/min. The chromatogram was divided into 15 broad fractions. Each broad fraction was accumulatively collected according to the method of Thompson et al. (1978).

A second fractionation was performed on all 15 broad fractions using a 1/8 in. o.d. × 12 ft stainless steel column

packed with 10% SP-1000 liquid stationary phase on 80/100 mesh Chromosorb W. A third preparative chromatography was performed on selected subfractions using a 1/8 in. o.d. × 12 ft stainless steel column packed with 10% OV-17 liquid stationary phase on 80/100 mesh Chromosorb W. A total of 420 relatively pure subfractions was collected and the aroma of each fraction was evaluated by a panel of four members.

**Identification of Gas Chromatographic Fractions.** The gas chromatographic fractions were identified by the combination of infrared and mass spectrometry, according to the procedure reported previously (Smouse and Chang, 1967).

Each fraction in sufficient quantity for infrared spectroscopy was analyzed on a Beckman IR-8 infrared spectrophotometer. A Hewlett-Packard instrument Model 5992 mass spectrometer with a splitter interfaced with a Hewlett-Packard 5730 gas chromatograph was used for GC-MS analysis. A 1/8 in. o.d. × 12 ft stainless steel column packed with 10% OV-17 was used for fractions which have been chromatographed two times, and a 1/8 in. × 12 ft stainless steel column packed with 10% SE-30 was used for fractions which have been fractionated three times. The flow rate was 28 mL/min and the column temperature was programmed to provide maximum resolution of each fraction analyzed.

## RESULTS AND DISCUSSION

Thirty-one pyrazines and three thiazoles are being reported as identified in the volatile flavor isolated from 540 lb of baked potatoes. Many of the pyrazines and thiazoles identified have never been reported before as volatile flavor components of baked potato or potato products (Table I).

Baked potato flavor is a very mild flavor but it is extremely complex. The total flavor yielded 420 fractions. In our opinion, the pyrazines and thiazoles were the most important compounds to the characteristic baked potato flavor. The results of this research indicate that a natural baked potato flavor is not due to a single compound, but is the result of the mixture of a number of components. The pyrazines and thiazoles thought to be important to the flavor of baked potato are listed in Table I. The compounds which are considered important contribute earthy, nutty, baked, sweet earthy, potato, and baked potato-like aromas. 2-Ethyl-6-vinylpyrazine was described as buttery, baked, and potato-like. 2-Ethyl-3-methylpyrazine contributes a pleasant earthy and nutty note to the total flavor. 2-Ethyl-3,6-dimethylpyrazine (Buttery et al., 1973) possessed an earthy, baked potato-like aroma and is very important to the flavor. The alkylated five- and six-membered bicyclic pyrazines, namely, 5-methyl-6,7-dihydro-5*H*-cyclopentapyrazine, 5,7-dimethyl-1,2,3,4,7,8-hexahydroquinoxaline, 2-methyl-6,7-dihydro-5*H*-cyclopentapyrazine, and 3,5-dimethyl-6,7-dihydro-5*H*-cyclopentapyrazine, contribute very pleasant earthy, baked, and potato-like aromas. 2,3-Dimethyl-5-butylpyrazine and 2,5-dimethyl-4-butylthiazole were characterized as having sweet earthy odors.

The results of this work indicate a similarity in odor for pyrazines and thiazoles with similar alkyl substituents. The dimethylbutyl trisubstituted thiazole and the dimethylbutyl trisubstituted pyrazines (with the butyl group adjacent to the nitrogen atom) have a sweet earthy aroma. Also, 2,5-diethyl-4-methylthiazole and 2,5-dimethyl-4-ethylthiazole were found to have odors very similar to the diethylmethyl and the dimethylethyl trisubstituted pyrazines.

The mechanisms by which pyrazines form in food have been reviewed previously (Maga and Sizer, 1973a; Walradt et al., 1971). The high content of amino acids and sugars in potato provide a reservoir of precursor compounds for the formation of pyrazines. The results of this research show the presence of a large number of pyrazines in baked potato flavor (31 identified in this work). There are more pyrazines in baked potato flavor than in other forms of cooked potato because of the presence of baked potato skins. Koehler et al. (1969) reports that temperatures

greater than 100 °C are needed for an appreciable rate of pyrazine formation. Because of the high water content of the potato, the temperature of the inside will remain too low for pyrazine formation. Most of the pyrazines form in the baked potato skins which dry out and reach temperatures high enough for the formation of pyrazine compounds.

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## LITERATURE CITED

- Bondarovich, H. A., Friedel, P., Krampfl, V., Renner, J. A., Shephard, F. W., Gianturco, M. A., *J. Agric. Food Chem.* **15**, 1093 (1967).
- Buttery, R. G., Seifert, R. M., Guadagni, D. G., Ling, L. C., *J. Agric. Food Chem.* **19**, 969 (1971).
- Buttery, R. G., Guadagni, D. G., Ling, L. C., *J. Sci. Food Agric.* **24**, 1125 (1973).
- Buttery, R. G., Ling, L. C., *J. Agric. Food Chem.* **21**, 745 (1973a).
- Buttery, R. G., Ling, L. C., Lundin, R. R., *J. Agric. Food Chem.* **21**, 488 (1973b).
- Chang, S. S., Vallese, F., Hwang, L. S., Hsieh, O., Min, D. B. S., *J. Agric. Food Chem.* **25**, 450 (1977).
- Deck, R. E., Chang, S. S., *Chem. Ind.*, 1343 (1965).
- Deck, R. E., Pokorny, J., Chang, S. S., *J. Food Sci.* **38**, 345 (1973).
- Friedel, P., Krampfl, V., Radford, T., Renner, J. A., Shephard, F. W., Gianturco, M. A., *J. Agric. Food Chem.* **19**, 530 (1971).
- Herz, K. O., Chang, S. S., *J. Food Sci.* **37**, 937 (1966).
- Kinlin, T. E., Muralidhara, R., Pittet, A. O., Sanderson, A., Walradt, J. P., *J. Agric. Food Chem.* **20**, 1021 (1972).
- Koehler, P. E., Mason, M. E., Newell, J. A., *J. Agric. Food Chem.* **17**, 393 (1969).
- Maga, J. A., Sizer, C. E., *J. Agric. Food Chem.* **21**, 22 (1973a).
- Maga, J. A., Sizer, C. E., *CRC Crit. Rev. Food Technol.*, 39 (1973b).
- Mason, M. E., Johnson, B., Hamming, M., *J. Agric. Food Chem.* **14**, 454 (1966).
- Pareles, S. R., Chang, S. S., *J. Agric. Food Chem.* **22**, 339 (1974).
- Pittet, A. O., Muralidhara, R., Walradt, J. P., Kinlin, T., *J. Agric. Food Chem.* **22**, 273 (1974).
- Seifert, R. M., Buttery, R. G., Guadagni, D. G., Black, D. R., Harris, J. G., *J. Agric. Food Chem.* **18**, 246 (1970).
- Smouse, T. H., Chang, S. S., *J. Am. Oil Chem. Soc.* **44**, 509 (1967).
- Thompson, J. A., May, W. A., Paulose, M. M., Peterson, R. J., Chang, S. S., *J. Am. Oil Chem. Soc.* **55**, 897 (1978).
- Walradt, J. P., Pittet, A. O., Kinlin, T. E., Muralidhara, R., Sanderson, A., *J. Agric. Food Chem.* **19**, 972 (1971).

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A Convenient Synthesis of (*E,E,Z*)-2,4,7-Decatrienal

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A convenient synthesis of (*E,E,Z*)-2,4,7-decatrienal in 42% yield from (*Z*)-hex-3-enol has been developed. The IR, MS, <sup>1</sup>H NMR spectra, odor threshold, and description of this compound are reported.

It is well known that oxidized lipids can produce off-aromas in food. Meijboom and Stroink (1972) reviewed

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the literature dealing with fishy off-aromas in food and reported the presence of (*E,E,Z*)-2,4,7-decatrienal in oxidized linolenic acid. They synthesized the dinitrophenylhydrazine (DNPH) derivatives of two isomers (*E,Z,Z* and *E,E,Z*) of 2,4,7-decatrienal using a seven-step synthesis. The present authors needed samples of (*E,E,Z*)-2,4,7-decatrienal to confirm the identity of a sus-