54-47-7; aspartate aminotransferase, 9000-97-9; aromatic amino acid aminotransferase, 37332-38-0.

LITERATURE CITED

- Bayoumi, R. A.; Rosalki, S. K. Clin. Chem. (Winston-Salem, N.C.) 1976, 22, 327–335.
- Brin, M.; Thiele, V. F. J. Nutr. 1967, 93, 213-221.
- Calbiochem LaJolla, CA, 1976, Document No. L03023.
- Crosby, W.; Munn, J. I.; Furth, F. W. U.S. Armed Forces Med. J. 1954, 5, 693–703.
- Davies, M. K.; Gregory, M. E.; Henry, K. M. J. Dairy Res. 1959, 26, 215–220.
- George, H.; Turner, R.; Gabay, S. J. Neurochem. 1967, 14, 841-845.
- Gregory, J. F. J. Food Sci. 1980a, 45, 84-86.
- Gregory, J. F. Anal. Biochem. 1980b, 102, 374-379.
- Gregory, J. F. J. Nutr. 1980c, 110, 995-1005.
- Gregory, J. F. J. Nutr. 1982, 112, 1643-1647.
- Gregory, J. F.; Kirk, J. R. J. Food Sci. 1978, 43, 1801-1815.
- Gregory, J. F.; Manley, D. B.; Kirk, J. R. J. Agric. Food Chem. 1981, 29, 921–927.
- Guilarte, T. R.; McIntyre, P. A.; Isan, M. F. J. Nutr. 1980, 110, 954–958.
- Hamm, M. W.; Mehansho, H.; Henderson, L. M. J. Nutr. 1979, 109, 1552–1559.
- Haskell, B. E.; Snell, E. E. Methods Enzymol. 1970, 18A, 512-519.
- Li, T. L.; Lumeng, L. "Methods in Vitamin B-6 Nutrition"; Plenum Press: New York, 1981; pp 289-296.
- Linkswiler, H.; Baumann, C. A.; Snell, E. E. J. Nutr. 1951, 43, 565–573.
- Lowry, O. H.; Rosebrough, N. J.; Farr, A. L.; Randall, R. J. J. Biol. Chem. 1951, 193, 265–275.
- Lui, A.; Minter, R.; Lumeng, L.; Li, T. K. Anal. Biochem. 1981, 112, 17-22.
- Lumeng, L.; Lui, A.; Li, T. K. "Methods in Vitamin B-6 Nutrition"; Plenum Press: New York, 1981; pp 57-67.
- Lumeng, L.; Ryan, M. P.; Li, T. K. J. Nutr. 1978, 108, 545-553.
- Matsuo, Y. J. Am. Chem. Soc. 1957, 79, 2016-2019.
- Mehansho, H.; Hamm, M. W.; Henderson, L. M. J. Nutr. 1979, 109, 1542–1551.
- Metzler, D. E.; Ikawa, M.; Snell, E. E. J. Am. Chem. Soc. 1954, 76, 648-652.

- Nguyen, L. B.; Gregory, J. F. J. Nutr. 1983, in press.
- Nguyen, L. B.; Gregory, J. F.; Damron, B. L. J. Nutr. 1981, 111, 1403-1420.
- Noguchi, T.; Okuno, E.; Minatogawa, Y.; Kido, R. Biochem. J. 1976, 155, 107-115.
- Noguchi, T.; Tokada, T. J. Biol. Chem. 1980, 255, 9844-9547.
- Neter, J.; Wasserman, W. "Applied Linear Statistical Models"; Richard D. Irwin, Inc.: Homewood, IL, 1974.
- Polansky, M. M. J. Am. Diet. Assoc. 1969, 54, 118-121.
- Polansky, M. M.; Murphy, E. W.; Toepfer, E. W. J. Assoc. Off. Agric. Chem. 1964, 47, 750–753.
- Raica, N.; Sauberlich, H. E. Am. J. Clin. Nutr. 1964, 15, 67-72. Sarma, P. S.; Snell, E. E.; Elvehjem, C. A. J. Biol. Chem. 1946,
- 165, 55–63.
- Skala, J. H.; Waring, P. P.; Lyons, M. F.; Rusnak, M. G.; Alletto, J. S. "Methods in Vitamin B-6 Nutrition"; Plenum Press: New York, 1981; pp 171-202.
- Sloger, M. S.; Reynolds, R. D. J. Nutr. 1980, 110, 1517-1524.
- Sloger, M. S.; Scholfield, L. G.; Reynolds, R. D. J. Nutr. 1978,
- 108, 1355-1360. Snell, E. E.; Haskell, B. E. Compr. Biochem. 1971, 21, 47-71.
- Tarr, J. B.; Tamura, T.; Stokstad, L. R. Am. J. Clin. Nutr. 1981,
- 34, 1328-1337. Thiele, V. F.; Brin, M. J. Nutr. 1968, 94, 237-242.
- Toepfer, E. W.; Lehmann, J. J. Assoc. Off. Agric. Chem. 1961,
- 44, 426-430.
- Vanderslice, J. T.; Maire, C. E.; Doherty, R. F.; Beecher, G. R. J. Agric. Food Chem. 1980, 28, 1145-1149.
- Waibel, P. E.; Cravens, W. W.; Snell, E. E. J. Nutr. 1952, 48, 531-538.
- Yen, J. T.; Jensen, A. H.; Baker, D. H. J. Anim. Sci. 1976, 42, 866-870.

Received for review December 2, 1982. Revised manuscript received May 23, 1983. Accepted July 10, 1983. This research was supported by Grant 4901-0410-9-0305-0 from the Competitive Research Grant Office, U.S. Department of Agriculture, Science and Education Administration. Florida Agricultural Experiment Stations Journal Series No. 4399.

Isolation and Identification of Volatile Compounds from Fried Chicken

Jian Tang,¹ Qi Zhang Jin,² Guo-Hui Shen,¹ Chi-Tang Ho,* and Stephen S. Chang

Volatile flavor compounds were isolated from 150 lb of fried chicken 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 gas chromatography-mass spectrometry. A total of 130 compounds were identified. The compounds identified in the volatiles of fried chicken included hydrocarbons, alcohols, aldehydes, ketones, acids, esters, pyrazines, pyridines, thiazoles, thiazolines, oxazoles, oxazolines, thiophenes, pyrroles, furans, a trithiolane, a trithiane, and thialdine.

Wilson and Katz (1972) reviewed the literature on chicken flavor and listed 178 compounds that had been reported in the volatiles from cooked chicken. Using GC-MS, Wilson and Katz (1972) identified 47 compounds in the volatiles of stewing chicken. The majority of these were saturated and unsaturated alcohols, aldehydes, and ketones. Janney et al. (1974) identified additional compounds, mainly aldehydes, ketones, and hydrocarbons, in freshly cooked fried chicken. In the analysis of boiling chicken broth, Horvat (1976) identified 53 compounds as its volatile constituents. A most recent review by Ramaswamy and Richards (1982) revealed that more than 250 compounds have been identified in the volatiles of poultry meat.

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

EXPERIMENTAL SECTION

Isolation of the Volatile Compounds from Fried Chicken. Fresh chicken breasts, with bones, purchased

Department of Food Science, Cook College, New Jersey Agricultural Experiment Station, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903.

¹Present address: Department of Chemical Engineering, Wuxi Institute of Light Industry, Wuxi, People's Republic of China.

²Present address: Scientific Research Institute of Fragrance and Flavor Industry, Ministry of Light Industry, Shanghai, People's Republic of China.

| | | mass | | | |
|--------------|-------------------------------------|-------------|--------------------|---|-----------|
| | | spec | | | |
| f | | tral | function | | mass |
| raction no a | identification | ence | no ^a | identification | reference |
| | | | | | |
| | Hydrocarbons | L | 5 0 | Pyrazines | |
| 2-2 | <i>n</i> -pentane | 0 b | 0-0 9-13 | pyrazine 2-methylpyrazine | e |
| 9-2 | n-dodecane | b | 10-10 | 2 3-dimethylpyrazine | e |
| 13-9 | <i>n</i> -tridecane | h | 10 - 11 | 2.5-dimethylpyrazine | e |
| 14-15 | <i>n</i> -tetradecane | b | 10-12 | 2.6-dimethylpyrazine | e |
| 18-3 | 2-methylhexadecane | \bar{b} | 12-11 | trimethylpyrazine | e |
| 18-3 | n-octadecane | b | 11-16 | isopropylpyrazine | е |
| 5-7 | 1-pentene | b | 11 - 14 | 2-methyl-3-ethylpyrazine | е |
| 6-8 | 2-pentene | b | 11-13 | 2-methyl-6-ethylpyrazine | е |
| 4-1 | 1-octene | b | 11-14 | 2-butylpyrazine | е |
| 3-2 | methylcyclohexane | b | 13-12 | 2,3-dimethyl-5-ethylpyrazine | е |
| 4-1 | 1,3-dimethylcyclonexane | 0 | 11-14 | 2,5-dimethyl-3-ethylpyrazine | e |
| 0-4 8-6 | limonene | 0 h | 12 - 13 13 - 14 | 2.0-diethylpyrazine 2.methyl 5.6-diethylpyrazine | e |
| 4-2 | henzene | h | 13 - 15 | 2-methyl-3 5-diethylpyrazine | e |
| 8-8 | <i>a</i> -xylene | b | 13-15 | 2-methyl-3-butylpyrazine | e |
| 6-4 | toluene | b | 11-17 | 2-methyl-5-vinylpyrazine | е |
| 12 - 17 | isopropylbenzene | b | 11-16 | 2-methyl-6-vinylpyr a zine | е |
| 10-10 | 1-methyl-3-propylbenzene | b | 11-16 | 2-isopropenylpyrazine | е |
| 11-11 | styrene | b | 13 - 21 | 6,7-dihydro-5 <i>H</i> -cyclopentapyrazine | f |
| 19-7 | 2,3-dihydro-1,1,3-trimethyl-3- | Ь | 14 - 22 | 2-methyl-6,7-dihydro-5 <i>H</i> - | f |
| | phenyl-1 <i>H</i> -indene | | | cyclopentapyrazine | |
| | Alcohols | | | Pyridines | |
| 3-4 | butanol | b | 13-6 | pyridine | b |
| 3-4 | 2-methylpropanol | b | 11-6 | 2-methylpyridine | b |
| 5-6 | pentanol | b | 10-13 | 3-ethylpyridine | b |
| 8-15 | hexanol | b | 11-13 | 4-ethylpyridine | b |
| 10-14 | neptanol | D h | 11-13 | 2-methyl-5-ethylpyridine | 0 |
| 10-13 | 6-methylhentan-3-ol | b | 11 - 14 19 - 10 | 2-butylpyridine | u b |
| 2-6 | 2-methyl-3-hutyn-2-ol | h | 12-10 13-17 | 2-partylpyridine | b |
| 11-24 | phenol | Ď | 10 1, | | Ŭ |
| 8-7 | cyclohexanol | b | 5 0 | Thiazoles | 1 |
| 13 - 22 | a-terpineol | b | 7-9 | thiazole | D T |
| 13-19 | 4-terpineol | b | 9-0 19-10 | 2-methyltniazole 2-methyl-4-othylthiazolo | g |
| | Aldehydes | | 12 - 19 19 - 17 | 2-methyl-5-ethylthiazole | 5 a |
| 3-5 | butanal | b | 11 - 12 | 2.4.5-trimethylthiazole | 5 g |
| 3-6 | 2-methylbutanal | b | 11-18 | 2.4-dimethyl-5-ethylthiazole | g g |
| 3-6 | 3-methylbutanal | b | 12 - 13 | 2-isopropyl-4,5-dimethylthiazole | ĥ |
| 4-3 | pentanal | b | 15 - 10 | 2,5-dimethyl-4-butylthiazole | Table II |
| 7-8 | hexanal | b | 15 - 7 | 2-isopropyl-4-ethyl-5-methylthiazole | Table II |
| 7-10 | heptanal | С | 14-15 | 2-butyl-4,5-dimethylthiazole | Table II |
| 8-11 | 2-isopropylbut-2-enal | С | 15-9 | 2-butyl-4-methyl-5-ethylthiazole | Table II |
| 7-6 | 4-methyl-2-pentenal | C | 16-8 | 2-pentyl-4,5-dimethylthiazole | Table II |
| 13-9 | 2-metnyl-2-neptenal hanzaldahyda | 0 h | 17-0 | 2-nexyl-4,5-dimethylthiazole | Table II |
| 11-10 | Denzaldenyde | 0 | 18-9 | 2-heptyl-4, 5-unnethylthiazole | Table II |
| | Ketones | | 18 - 10 | 2-octyl-4.5-dimethylthiazole | Table II |
| 3-3 | 2-butanone | 6 | | | |
| 4-2 | 2-pentanone | <i>b</i> | 10 10 | Thiazolines | 2 |
| 8-10 | 2-neptanone | 0 h | 10-13 | 2,4-almethyl-3-thiazoline | l i |
| 0-11 9_8 | 6-methylbent-5-en-3-one | d | 10-13 | 2,4,5-thmethyf-5-thazonne | 1 |
| 00 | | u | | Furans | |
| 0.0 | Acids and Esters | , | 8-8 | 2-butylfuran | h |
| 3-3 8-1 | 2-metnyiputanoic acid | 0 b | 11-6 | z-pentynuran 2-bexylfuran | n h |
| 3-3 | pentanoic acid | h | 13-19 | 2-heptylfuran | ĥ |
| 12-19 | hexanoic acid | \tilde{b} | 14-15 | 2-octylfuran | h |
| 2-2 | ethyl acetate | b | 11 - 20 | furfuryl alcohol | h |
| 18 - 14 | diethyl phthalate | d | 8-13 | 2-methyltetrahydrofuran-3-one | k |
| | Oxazoles | | - | Miscellaneous Sulfur-Containing Compour | ıds |
| 6-7 | 4,5-dimethyloxazole | g | 13-19 | 3,5-dimethyl-1,2,4-trithiolane | ь |
| 8-11 | 2,4,5-trimethyloxazole | g | 16-13 | 2,4,6-trimethyl-1,3,5-trithiane | Ь |
| 10-10 | 2-isopropyl-4,5-dimethyloxazole | h | 14-23 | thialdine | j |
| | Oxazolines | | | Miscellaneous Compounds | |
| 6-6 | 2, 4-dimethyl- 3 -oxazoline | i | 11-14 | <i>o</i> -dichlorobenzene | b |
| 6-6 | 2, 4, 5-trimethyl-3-oxazoline | i | 5-4 | 1,4-dioxane | b |
| | Thiophenes | | 4-1 | acetaldehyde diethyl acetal | d |
| 6-5 | 2-methylthiophene | b | | Pyrroles | |
| 13-6 | 2-isopropylthiophene | b | 7 - 14 | pyrrole b | |

 Table I (Continued)

| fraction no. ^a | identification | mass spec- tral refer- f ence | fraction no. ^a | identification | mass spectral reference |
|------------------------------|-------------------|---|------------------------------|-----------------------|-------------------------------|
| 10-10 | 2-acetylthiophene | h | 8-7 | 2-methylpyrrole | h |
| 11-13 | 2-butylthiophene | Ь | 13-28 | 2-acetylpyrrole | j |
| | 2-pentylthiophene | | 12-18 | 2-isobutylpyrrole | k |
| | | | 10-10 | N-isobutylpyrrole | j |
| | | | 13-24 | N-(2-butanoyl)pyrrole | j |

^a The first and second numerals indicate the position of the GC fraction during the first and second chromatographies, respectively. ^b Heller and Milne (1978). ^c Buttery (1973). ^d MSDC (1974). ^e Maga and Sizer (1973). ^f Pittet et al. (1974). ^g Vitzthum and Werkhoff (1974). ^h ten Noever de Brauw et al. (1980). ⁱ Mussinan et al. (1976). ^j Vernin (1982a). ^k Kinlin et al. (1972).

from a local supermarket were cut into 1.5-2 in. cubes, coated with 2% flour, and fried in Fri-al shortening (containing 90% beef fat and 10% cottonseed oil) (Intercon Co., New Jersey) at 185 °C in air for 8 min. Fried chicken was prepared by using a Cecilware Model ELK-250 electric fryer. The volatile flavor compounds of fried chicken were isolated by the apparatus previously described by Chang et al. (1977). Nitrogen gas was used to remove the volatile compounds from the fried chicken. The sample and nitrogen gas were kept at 85 °C during the isolation period. Twenty-five pounds of fried chicken was used for each isolation, which lasted 48 h. A total of six batches 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 a 30-plate Oldershaw column and a 200-plate spinning band still.

Fractionation of the Flavor Isolate. The fried chicken flavor isolate was fractionated in a manner similar to that described by Coleman et al. (1981). The initial perparative chromatography of the fried chicken flavor isolate was performed on a Hewlett-Packard 5840A gas chromatograph equipped with a flame ionization detector (FID), fitted with a $^{1}/_{8}$ in. o.d. × 12 ft stainless steel column packed with 10% OV-17 on 60–80-mesh Chromosorb W D.M.C.S. The flow rate was 30 mL/min with a column temperature that was held at 50 °C for 3 min and then increased by 3 °C/min to a holding temperature of 220 °C. The chromatogram (Figure 1) was divided into 19 broad fractions. Each broad fraction was successfully collected according to the method of Thompson et al. (1978).

A second fractionation was performed on all 19 fractions using a $1/_8$ in. o.d. × 12 ft stainless steel column packed with 10% OV-351 on 60–80-mesh Supelcoport.

GC-MS Analysis of Fractions. 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 Supelcoport. The ionization voltage of the mass spectrometer was 70 eV.

Synthesis of Authentic Alkylthiazoles. Authentic alkylthiazoles were synthesized by the method of Kurkjy and Brown (1952) by the addition of the corresponding α -bromo ketone to the preformed thioamide. Yields were all quite satisfactory at about 50%. The steam distilled products were purified by GC using a $^{1}/_{8}$ in. o.d. \times 12 ft stainless steel column packed with 10% SP-1000 on 80– 100-mesh Chromosorb W. The purified thiazoles were

then subjected to GC-MS analysis.

RESULTS AND DISCUSSION

The volatiles with a genuine flavor of the original fried chicken were isolated from a relatively large amount (150 lbs) of fried chicken. A preliminary gas chromatogram of the volatile flavor compounds of fried chicken (on an OV-17 column) is shown in Figure 1. Each fraction was sensory evaluated by two expert flavorists. Three fractions, fractions 11, 13, and 14, were determined as being the important flavor of fried chicken. They had a fried, fatty, and chicken-like aroma.

A total of 130 compounds (Table I) was identified in the volatiles of fried chicken. The volatile flavor compounds that contribute to fried chicken flavor may be formed from (1) constituents of the chicken during the frying process, (2) constituents of the flour during the frying process, (3) thermal and oxidative decomposition of the frying fat itself, and (4) the interaction of decomposition products from the chicken or flour and the frying fat.

Hydrocarbons, Alcohols, and Carbonyl Compounds. α -Pinene, limonene, α -terpineol, and 4-terpineol identified are common constituents of essential oils (Ohloff, 1978). They may be the components originally presented in flour. Wilson and Katz (1972) reported the identification of α -terpineol in the volatiles isolated from aqueous cooked chicken broth and suggested that it is systemic introduction from the feed.

2-Isopropylbut-2-enal and 4-methyl-2-pentenal identified in fried chicken flavor have been identified in the volatiles of potato chips (Buttery, 1973). These compounds are probably formed in the fried chicken during the frying by aldol-type condensations.

Pyrazines. Of the 21 alkylpyrazines identified in fried chicken flavor, only 2-methylpyrazine has been reported in aqueous cooked chicken flavor (Wilson and Katz, 1972; Horvat, 1976). The higher temperature of frying probably favors the formation of pyrazines. Koehler et al. (1969) reports that temperatures greater than 100 °C are needed for an appreciable rate of pyrazine formation. Alkylpyrazines identified may also come from the frying of flour. Alkylpyrazines frequently have roasted, nutty, green, or earthy qualities (MacLeod and Seyyedain-Ardebili, 1981). The mechanisms by which pyrazines formed in food flavor have been reviewed previously (Maga and Sizer, 1973; Maga, 1982).

Pyridines. Compared to other important classes of compounds associated with food flavor, relatively few pyridines have been identified as being naturally occurring (Maga, 1981a). Their occurrences in food and their formation pathways have been reviewed by Maga (1981a) and Vernin (1982b). 2-Methylpyridine has been reported

Table II. Mass Spectral and Sensory Data of Synthetic Authentic Thiazoles Identified in Fried Chicken Flavor

| compound | odor description | characteristic MS data, m/z (rel intensity) |
|---|---|---|
| 2,5-dimethyl-4-butylthiazole (C ₉ H ₁₅ NS) | fruity, some spicy background | 27 (8), 29 (3), 41 (10), 45 (12), 53 (4), 59 (22), 65 (2), 71 (5), 85 (33), 86 (6), 95 (1), 99 (2), 112 (1), 113 (2), 126 (21), 127 (100), 140 (10), 141 (4), 154 (11), 155 (1), 169 (12), 170 (3): $M = 169$ |
| 2-isopropyl-4-ethyl-5-methylthiazole $(C_{9}H_{15}NS)$ | raw sweet potato | 27 (40), 28 (33), 39 (44), 41 (50), 56 (19), 59 (62), 67 (18), 71 (10), 85 (60), 86 (5), 99 (12), 100 (20), 111 (2), 126 (4), 127 (11), 139 (7), 141 (4), 154 (100), 155 (13), 168 (19), 169 (50): M = 169 |
| 2-butyl-4,5-dimethylthiazole (C ₉ H ₁₅ NS) | green, vegetable | $\begin{array}{c} (10), 129 (30), 41 (8), 45 (9), 53 (8), 59 (9), 68 \\ (2), 71 (18), 85 (9), 86 (16), 112 (1), 113 (1), \\ 126 (18), 127 (100), 140 (19), 141 (6), 154 \\ (5), 169 (7), 170 (2); M = 169 \end{array}$ |
| 2-butyl-4-methyl-5-ethylthiazole $(C_{10}H_{17}NS)$ | green, mellon, pleasant vegetable green note | 27 (23), 28 (20), 41 (24), 45 (36), 53 (6), 55 (6), 67 (10), 71 (43), 84 (6), 85 (8), 99 (5), 100 (3), 112 (14), 113 (9), 125 (4), 126 (2), 141 (100), 142 (11), 154 (23), 155 (41), 168 (14), 169 (2), 182 (6), 183 (5); $\mathbf{M} = 183$ |
| 2-pentyl-4,5-dimethylthiazole (C ₁₀ H ₁₇ NS) | green, vegetable | 27 (13), 29 (8), 41 (13), 45 (12), 53 (10), 59 (11), 68 (2), 71 (19), 85 (9), 86 (17), 94 (1), 112 (1), 113 (1), 126 (16), 127 (100), 140 (29), 141 (9), 154 (11), 155 (2), 168 (1), 182 (1) 183 (7): M = 183 |
| 2-hexyl-4,5-dimethylthiazole $(C_{11}H_{19}NS)$ | green, vegetable, oily | (1), 10, (1), 11, 11, 11, 12, 12, 12, 12, 12, 12, 12 |
| 2-heptyl-4,5-dimethylthiazole | very strong spicy, sulfury | $\begin{array}{l} (2), (2), (2), (1), (4), (3), (1), (1), (1), (2), (2), (2), (2), (2), (2), (2), (2$ |
| $\begin{array}{l} 2\text{-heptyl-4-ethyl-5-methylthiazole} \\ (C_{13}H_{23}NS) \end{array}$ | sweet, fruity, fatty coconut, pleasant | $\begin{array}{l} 27 \ (9), \ 29 \ (10), \ 39 \ (8), \ 41 \ (18), \ 53 \ (4), \ 59 \ (17), \\ 65 \ (3), \ 67 \ (6), \ 79 \ (11), \ 85 \ (15), \ 99 \ (3), \ 100 \\ (4), \ 113 \ (1), \ 126 \ (4), \ 128 \ (2), \ 140 \ (9), \ 141 \\ (100), \ 154 \ (25), \ 155 \ (8), \ 168 \ (5), \ 169 \ (1), \\ 182 \ (3), \ 196 \ (6), \ 197 \ (1), \ 210 \ (1), \ 224 \ (2), \\ 225 \ (6); \ M = \ 225 \end{array}$ |
| 2-octyl-4,5-dimethylthiazole ($C_{13}H_{23}NS$) | weak, little sweet fatty | 27 (1), 29 (14), 41 (18), 45 (17), 53 (8), 55 (6), 65 (2), 71 (11), 85 (7), 86 (5), 99 (2), 112 (3), 114 (2), 127 (100), 128 (9), 140 (27), 141 (7), 154 (5), 155 (1), 168 (2), 182 (6), 183 (1), 196 (3), 197 (1), 210 (1), 224 (1), 225 (3): $M = 225$ |

^a The two most intense ions every 14 mass units above 20 are listed.



Figure 1. Gas chromatographic fraction of fried chicken flavor (OV-17 column).

previously (Horvat, 1976) in the volatiles of cooked chicken. Few organoleptic data are available for pyridine derivatives. According to Pittet and Hruza (1974), 2-alkylpyridines possess a green odor.

Due to the lack of reference mass spectral data, many alkylpyridines present in the volatiles of fried chicken cannot be identified at the present time.

Thiazoles and Thiazolines. Sixteen thiazoles and two thiazolines identified in this study are all new to the flavor of cooked chicken. Nine of the thiazoles identified are new volatile components of foods. They were identified by comparing their mass spectra with that of authentic synthetic compounds. Table II lists the mass spectra of the alkylthiazoles synthesized by using the method of presentation of Herz et al. (1971).

Numerous thiazoles were reported in volatiles of a wide variety of foods such as heated beef (Chang and Peterson, 1977), coffee (Vitzthum and Werkhoff, 1974), baked potato (Coleman et al., 1981), roasted peanuts (Ho et al., 1982), and fried bacon (Ho et al., 1983). Alkylthiazoles have a green, nutty, and vegetable-like aroma (Ohloff and Flament, 1979). 2-Heptyl-4-ethyl-5-methylthiazole and 2octyl-4,5-dimethylthiazole synthesized have a sweet fatty aroma. However, 2-heptyl-4,5-dimethylthiazole synthesized has a very strong spicy, sulfury note. Thiazoles in foods may be formed as a result of interactions of sulfur-containing amino acids with carbohydrates or carbonyls (Ohloff and Flament, 1979).

2,4-Dimethyl-3-thiazoline and 2,4,5-trimethyl-3-thiazoline identified in this study have been reported in the volatiles of cooked beef (Mussinan et al., 1976). 2,4-Dimethyl-3-thiazoline has also been reported in the volatiles of roasted peanuts (Buckholz and Daun, 1981) and in the reaction mixture of glucose with hydrogen sulfide and ammonia (Shibamoto and Russell, 1977). 2,4-Dimethyl-3-thiazoline was described as nutty, roasted, and vegetable-like, while 2,4,5-trimethyl-3-thiazoline was described as meaty, nutty, and onion-like (Mussinan et al., 1976).

Oxazoles and Oxazolines. The occurrence of oxazoles in food flavor has been reviewed (Maga, 1981b). Most recently, oxazoles had been identified in baked potato (Coleman et al., 1981), roasted peanuts (Ho et al., 1982), and fried bacon (Ho et al., 1983). 4,5-Dimethyloxazole and 2,4,5-trimethyloxazole identified in fried chicken flavor had been found in the reaction mixture of L-cysteine and diacetyl (Ho and Hartman, 1982).

2,4,5-Trimethyl-3-oxazoline identified in this study was first reported by Chang et al. (1968) in the flavor of boiled beef. 2,4-Dimethyl-3-oxazoline identified had been reported in cooked beef (Mussinan et al., 1976) and fried bacon (Ho et al., 1983) and was described as nutty and vegetable-like.

Thiophenes. Of the five thiophenes identified in this study, 2-acetylthiophene and 2-methylthiophene had previously been reported in the volatiles of cooked chicken (Ramaswamy and Richards, 1982). Thiophenes have been identified in large numbers in the flavor of meat-related products (Ohloff and Flament, 1979). A recently published review gave interesting details on the role of thiophenes in foodstuffs (Maga, 1975).

Other Heterocyclic Compounds. Six pyrroles identified in this study are all new to the flavor of cooked chicken. The occurrences of pyrroles in foods and model systems have recently been reviewed (Maga, 1981c).

Due to their wide distribution, furanoids play an important role in food flavor. Five 2-alkylfurans identified in this study were probably formed through the thermal oxidation of lipids. 2-Pentylfuran, presumably formed by autoxidation of linoleate, imparted a beany and grassy flavor impression when added to vegetable oil at a concentration up to 10 ppm (Smouse and Chang, 1967).

3,5-Dimethyl-1,2,4-trithiolane, 2,4,6-trimethyl-1,3,5trithiane, and thialdine identified in fried chicken flavor are probably formed through the interaction of acetaldehyde, hydrogen sulfide, and ammonia (Takken et al., 1976). 3,5-Dimethyl-1,2,4-trithiolane, first identified by Chang et al. (1968), had been previously reported in cooked chicken (Horvat, 1976). Thialdine (2,4,6-trimethyl-5,6dihydro-1,3,5-dithiazine) identified for the first time in the volatiles of chicken had been reported in the flavor of cooked beef (Wilson et al., 1973). According to the patent literature (Wilson et al., 1974), 2,4,6-trimethyl-1,3,5-trithiane and thialdine are useful for chicken flavor.

ACKNOWLEDGMENT

We thank Joan B. Shumsky for her secretarial aid.

Registry No. Pentane, 109-66-0; undecane, 1120-21-4; dodecane, 112-40-3; tridecane, 629-50-5; tetradecane, 629-59-4; 2methylhexadecane, 1560-92-5; octadecane, 593-45-3; 1-pentene, 109-67-1; 2-pentene, 109-68-2; 1-octene, 111-66-0; methylcyclohexane, 108-87-2; 1,3-dimethylcyclohexane, 591-21-9; α -pinene, 80-56-8; limonene, 138-86-3; benzene, 71-43-2; o-xylene, 95-47-6; toluene, 108-88-3; isopropylbenzene, 98-82-8; 1-methyl-3propylbenzene, 1074-43-7; styrene, 100-42-5; 2,3-dihydro-1,1,3trimethyl-3-phenyl-1H-indene, 3910-35-8; butanol, 71-36-3; 2methylpropanol, 78-83-1; pentanol, 71-41-0; hexanol, 111-27-3; heptanol, 111-70-6; octanol, 111-87-5; 6-methylheptan-3-ol, 18720-66-6; 2-methyl-3-butyn-2-ol, 115-19-5; phenol, 108-95-2; cyclohexanol, 108-93-0; α -terpineol, 98-55-5; 4-terpineol, 562-74-3; butanal, 123-72-8; 2-methylbutanol, 96-17-3; 3-methylbutanol, 590-86-3; pentanal, 110-62-3; hexanal, 66-25-1; heptanal, 111-71-7; 2-isopropylbut-2-enal, 40878-71-5; 4-methyl-2-pentenal, 5362-56-1; 2-methyl-2-heptenal, 623-36-9; benzaldehyde, 100-52-7; 2-butanone, 78-93-3; 2-pentanone, 107-87-9; 2-heptanone, 110-43-0; 2-methylcyclopentanone, 1120-72-5; 6-methylhept-5-en-3-one, 86883-66-1; 2-methylbutanoic acid, 116-53-0; 3-methylbutanoic acid, 503-74-2; pentanoic acid, 109-52-4; hexanoic acid, 142-62-1; ethyl acetate, 141-78-6; diethyl phthalate, 84-66-2; pyrazine, 290-37-9; 2-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; isopropylpyrazine, 29460-90-0; 2-methyl-3-ethylpyrazine, 15707-23-0; 2-methyl-6ethylpyrazine, 13925-03-6; 2-butylpyrazine, 29460-91-1; 2,3-dimethyl-5-ethylpyrazine, 15707-34-3; 2,5-dimethyl-3-ethylpyrazine, 13360-65-1; 2,6-diethylpyrazine, 13067-27-1; 2-methyl-5,6-diethylpyrazine, 18138-04-0; 2-methyl-3,5-diethylpyrazine, 18138-05-1; 2-methyl-3-butylpyrazine, 15987-00-5; 2-methyl-5-vinylpyrazine, 13925-08-1; 2-methyl-6-vinylpyrazine, 13925-09-2; 2isopropenylpyrazine, 38713-41-6; 6,7-dihydro-5H-cyclopentapyrazine, 23747-47-9; 2-methyl-6,7-dihydro-5H-cyclopentapyrazine, 23747-46-8; pyridine, 110-86-1; 2-methylpyridine, 109-06-8; 3ethylpyridine, 536-78-7; 4-ethylpyridine, 536-75-4; 2-methyl-5ethylpyridine, 104-90-5; 2-ethyl-3-methylpyridine, 56986-88-0; 2-butylpyridine, 5058-19-5; 2-pentylpyridine, 2294-76-0; thiazole, 288-47-1; 2-methylthiazole, 3581-87-1; 2-methyl-4-ethylthiazole, 32272-48-3; 2-methyl-5-ethylthiazole, 19961-52-5; 2,4,5-trimethylthiazole, 13623-11-5; 2,4-dimethyl-5-ethylthiazole, 38205-61-7; 2-isopropyl-4,5-dimethylthiazole, 53498-30-9; 2,5-dimethyl-4-butylthiazole, 41981-77-5; 2-isopropyl-4-ethyl-5methylthiazole, 87116-68-5; 2-butyl-4,5-dimethylthiazole, 76572-48-0; 2-butyl-4-methyl-5-ethylthiazole, 86290-20-2; 2-pentyl-4,5dimethylthiazole, 86290-22-4; 2-hexyl-4,5-dimethylthiazole, 87262-49-5; 2-heptyl-4,5-dimethylthiazole, 87262-50-8; 2-heptyl-4-ethyl-5-methylthiazole, 87262-51-9; 2-octyl-4,5-dimethylthiazole, 87262-52-0; 2,4-dimethyl-3-thiazoline, 60755-05-7; 2,4,5-trimethyl-3-thiazoline, 60633-24-1; 4,5-dimethyloxazole, 20662-83-3; 2,4,5-trimethyloxazole, 20662-84-4; 2-isopropyl-4,5-dimethyloxazole, 19519-45-0; 2,4-dimethyl-3-oxazoline, 77311-02-5; 2,4,5trimethyl-3-oxazoline, 22694-96-8; 2-methylthiophene, 554-14-3; 2-isopropylthiophene, 4095-22-1; 2-acetylthiophene, 88-15-3; 2butylthiophene, 1455-20-5; 2-pentylthiophene, 4861-58-9; pyrrole, 109-97-7; 2-methylpyrrole, 636-41-9; 2-acetylpyrrole, 1072-83-9; 2-isobutylpyrrole, 38954-30-2; N-isobutylpyrrole, 20884-13-3; 2-butylfuran, 4466-24-4; 2-pentylfuran, 3777-69-3; 2-hexylfuran, 3777-70-6; 2-heptylfuran, 3777-71-7; 2-octylfuran, 4179-38-8; furfuryl alcohol, 98-00-0; 2-methyltetrahydrofuran-3-one, 3188-00-9; 3,5-dimethyl-1,2,4-trithiolane, 23654-92-4; 2,4,6-trimethyl-1,3,5-trithiane, 2765-04-0; thialdine, 638-17-5; o-dichlorobenzene, 95-50-1; 1,4-dioxane, 123-91-1; acetaldehyde diethyl acetal, 105-57-7.

LITERATURE CITED

Buckholz, L. L.; Daun, H. ACS Symp. Ser. 1981, No. 170, 163. Buttery, R. G. J. Agric. Food Chem. 1973, 21, 31.

- 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.; Valese, 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.
- Heller, S. R.; Milne, G. W. A. "EPA-NIH Mass Spectral Data Base"; U.S. Government Printing Office: Washington, DC, 1978.
- Herz, H. S.; Hites, R. A.; Biemann, K. Anal. Chem. 1971, 43, 681.
- Herz, K. O.; Chang, S. S. J. Food Sci. 1966, 31, 937.
- Ho, C.-T.; Hartman, G. J. J. Agric. Food Chem. 1982, 30, 793.
- Ho, C.-T.; Lee, K. N.; Jin, Q. Z. J. Agric. Food Chem. 1983, 31, 336.
- Ho, C.-T.; Lee, M.-H.; Chang, S. S. J. Food Sci. 1982, 47, 127.
- Horvat, R. J. J. Agric. Food Chem. 1976, 24, 953.
- Janney, C. G.; Hale, K. K.; Higman, H. C. Poult. Sci. 1974, 53, 1758.
- Kinlin, T. E.; Muralidhara, R.; Pittet, A. O.; Sanderson, A.; Waldradt, J. P. J. Agric. Food Chem. 1972, 20, 1021.
- Koehler, P. E.; Mason, M. E.; Newell, J. A. J. Agric. Food Chem. 1969, 17, 393.
- Kurkjy, R. P.; Brown, E. V. J. Am. Chem. Soc. 1952, 74, 5778.
- MacLeod, G.; Seyyedain-Ardebili, M. CRC Crit. Rev. Food Sci. Nutr. 1981, 14, 438.

- Maga, J. A. CRC Crit. Rev. Food Sci. Nutr. 1975, 6, 241.
- Maga, J. A. J. Agric. Food Chem. 1981a, 29, 895.
- Maga, J. A. CRC Crit. Rev. Food Sci. Nutr. 1981b, 12, 295.
- Maga, J. A. J. Agric. Food Chem. 1981c, 29, 691.
- Maga, J. A. CRC Crit. Rev. Food Sci. Nutr. 1982, 15, 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.; Wilson, R. A.; Katz, I.; Hruza, A.; Vock, M. H. ACS Symp. Ser. 1976, No. 26, 133.
- Ohloff, G. Fortschr. Chem. Org. Naturst. 1978, 35, 431.
- Ohloff, G.; Flament, I. Fortschr. Chem. Org. Naturst. 1979, 36, 231.
- Pittet, A. O.; Hruza, D. E. J. Agric. Food Chem. 1974, 22, 264.
- Pittet, A. O.; Muralidhara, R.; Walradt, J. P.; Kinlin, T. J. Agric. Food Chem. 1974, 22, 273.
- Ramaswamy, H. S.; Richards, J. F. Can. Inst. Food Sci. Technol. J. 1982, 15, 7.
- Shibamoto, T.; Russell, G. F. J. Agric. Food Chem. 1977, 25, 110. Smouse, T. H.; Chang, S. S. J. Am. Oil Chem. Soc. 1967, 44, 509.

- Takken, H. J.; Van der Linde, L. M.; De Valois, P. J.; Van Dort, H. M.; Boelens, M. ACS Symp. Ser. 1976, No. 26, 114.
- ten Noever de Brauw, M. C.; Bouwman, J.; Tas, A. C.; La Vos, 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.
- Vernin, G. "The Chemistry of Heterocyclic Flavoring and Aroma Compounds"; Ellis Horwood, Ltd.: Chichester, England, 1982a.
- Vernin, G. Perfum. Flavor. 1982b, 7 (5), 23.
- Vitzthum, O. G.; Werkhoff, P. J. Agric. Food Chem. 1974, 39, 1210.
- Wilson, R. A.; Katz, I. J. Agric. Food Chem. 1972, 20, 741. Wilson, R. A.; Mussinan, C. J.; Katz, I.; Sanderson, A. J. Agric.
- Food Chem. 1973, 21, 873. Wilson R. A. Vock M. H. Katz, L. Shustor, S. I. British Patent
- Wilson, R. A.; Vock, M. H.; Katz, I.; Shuster, S. J. British Patent 1 364 747, 1974.

Received for review February 14, 1983. Revised manuscript received June 29, 1983. Accepted August 24, 1983. New Jersey Agricultural Experiment Station, Publication No. D-10501-1-83, supported by State Funds.

Biological and Biochemical Changes in Two Nigerian Species of Sorghum (SK.5912 and HP3) following Premalting- γ -Irradiation Treatment

A. O. Uwaifo

Two Nigerian species of sorghum—Sorghum acaudatum (SK.5912) and Sorghum guineense (HP3)—were γ -irradiated prior to malting on a Cobalt irradiator. The species were exposed to the following doses—0.22, 0.44, 1.76, and 4.95 krd—in the assays for diastatic power, β -amylase, and α -amylases, while in the assays for germinative energy and lengths of rootlets and acrospire they were exposed to a dose range of 0–5 krd. A dose of 1.76 krd raised the diastatic power, β -amylase, α -amylase, germinative energy, and lengths of rootlets and acrospire they use exposed to a dose range of 0–5 krd. A dose of 1.76 krd raised the diastatic power, β -amylase, α -amylase, germinative energy, and lengths of rootlets and acrospire maximally relative to those of the unirradiated sorghum in the species studied. This effect of 1.76 krd was, however, higher in SK.5912 species than in HP3 species. This dose also raised DNA levels in the two species relative to that of the unirradiated species but had the reverse effect on protein levels in the two species.

 γ -Irradiation has been reported to have predilection for proteins, enzymes, DNA, RNA, amino acids, and nucleoproteins in its effects on biological materials (EL-Meteiny et al., 1973).

The nature and degree of these effects are dose dependent (Holms, 1957). γ -Irradiation effects on barley is one of those most extensively studied (Tipples and Norris, 1963; Adams and Nilan, 1958) to date, this being so because of its utilization in the manufacture of beer.

In this study the results obtained when two sorghum species are exposed to different doses of γ -irradiation prior to malting are presented. The biological and biochemical parameters monitored after irradiation and subsequent malting include (i) DNA levels, (ii) diastatic power, (iii) β -amylase and (iv) α -amylase activities, (v) protein levels, (vi) germinative energy, (vii) length of rootlets, and (viii) length of acrospire.

MATERIALS AND METHODS

 γ -Irradiation. A total of 75 g of sorghum devoid of extraneous particles (stones and broken seeds) was placed in a glass receptacle provided along with the irradiator (⁶⁰Co γ irradiator, Model 3500, Noratom-Norcontrol A/S,

Holmenveien 20, Oslo 3, Norway) and irradiated at a dose rate of 400 ± 40 rd/min at room temperature (25 ± 2 °C). The effective doses to which the sorghum species were exposed in the different assays are shown in the figures for these assays.

Malting. The γ -irradiated and unirradiated sorghum were malted along the lines outlined in the work of Dyer and Novellie (1966).

Determination of the Activities of the Amylases and Diastatic Power. β -Amylases was determined in the malted γ -irradiated and unirradiated sorghum species by the method outlined in the work of Kneen and Sandstedt (1941) while α -amylase in the two species of sorghum was determined by the method of Meredith (1976). The diastatic power of irradiated and unirradiated sorghum species was determined by the method of Novellie (1962).

Determination of DNA and Protein. DNA was assayed by the diphenylamine method of Burton (1956) and protein by the method of Lowry et al. (1951). Bovine serum albumin BSA (SIGMA) and crystalline DNA (Sigma) were used as standards in the assays.

RESULTS

As depicted in Figure 1, 2.0 krd seems to have elevated maximally the germinative energy and growth of rootlets in sorghum species SK.5912 and HP3. Growth in the two

Oncology and Microbiology Section, Department of Biochemistry, University of Ibadan, Ibadan, Nigeria.