

0.998 linear coefficient for both compounds ($\mu\text{g}\cdot\text{g}^{-1}$, soil vs. integration ratios GLYPH/IS or AMPA/IS). The analyses of one single sample starting from the soil extraction takes about 3 h. The process can easily be adapted for simultaneous analyses of many samples, and routinely eight samples a day have been analyzed.

This procedure offers a simple, sensitive, and reproducible determination of GLYPH and AMPA at residue levels in soils of very different character in a single operation. It is also applicable to water samples and most probably, perhaps after some modification, to other types of materials.

Registry No. Glyphosphate, 1071-83-6; $\text{NH}_2\text{CH}_2\text{PO}_3\text{H}_2$, 1066-51-9.

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Characterization of Volatile Compounds Generated from the Reactions of Aldehydes with Ammonium Sulfide

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Volatile compounds generated from the reactions of selected aldehydes with ammonium sulfide were characterized by GC-MS. The mass spectral data from 2-pentyl-3,5-dibutylpyridine, 3-methyl-5-butyl-1,2,4-trithiolane, and 3-methyl-5-pentyl-1,2,4-trithiolane allowed us to identify these compounds in fried chicken or french-fried potato flavor.

INTRODUCTION

Previous studies in our laboratory reported the identification of 130 compounds from fried chicken flavor (Tang et al., 1983) and 427 compounds from french-fried potato flavor (Carlin, 1983). Due to the lack of reference mass spectral data a large number of compounds from these studies remain unidentified.

The compounds identified in fried chicken and french-fried potato flavors were postulated to form primarily through the nonenzymatic browning reactions, degradation of sugars, thermal and oxidative decomposition of lipids, and lipid-protein interactions. In addition, the structures of several compounds identified suggested that they were formed from reactions between degradation products.

Shu et al. (1980, 1981, 1985) examined reactions between degradation products. They characterized the volatile compounds generated from the reaction of isovaleraldehyde and ammonium sulfide. Mass spectral data from this work allowed us to identify 3,5-diisobutyl-1,2,4-trithiolane and 2-isobutyl-3,5-diisopropylpyridine in fried chicken flavor (Hartman et al., 1984).

We subsequently conducted our own reaction experiments in order to understand the generation of volatile compounds in fried chicken and french-fried potato flavors and to assist in the identification of unknown mass spectra from these previous studies. This paper reports the characterization of volatile compounds generated from the reactions of selected aldehydes with ammonium sulfide.

EXPERIMENTAL SECTION

Preparation of Reaction Mixtures. I. Reaction of Pentanal or Hexanal with Ammonium Sulfide. Pentanal or hexanal was mixed with aqueous 22% ammonium sulfide (Mallinckrodt, Inc., St. Louis, MO) in a 1:1 molar ratio at room temperature for 2 h. The reaction mixture was vacuum steam distilled (0.3 mmHg). The distillate was condensed by a four-stage cold-finger trapping sequence cooled with dry ice-acetone slurries (-70°C). The aqueous distillate was saturated with NaCl and extracted with redistilled diethyl ether. The ether extracts were back-washed with water and dried over anhydrous sodium sulfate. The ether extracts were concentrated on a spinning-band distillation apparatus.

II. Reaction of Pentanal, Isopentanal, or Hexanal with Acetaldehyde and Ammonium Sulfide. Pentanal, isopentanal, or hexanal was mixed with acetaldehyde and aqueous 22% ammonium sulfide in a 1:1:2 molar ratio at room temperature for 2 h. The reaction mixture was vacuum steam distilled, extracted with diethyl ether, dried, and concentrated as previously described.

III. Reaction of β -Mercaptoacetaldehyde and Ammonium Sulfide. β -Mercaptoacetaldehyde in the form of its

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Table I. Volatile Products Generated from the Reaction of Pentanal and Ammonium Sulfide

| product | % vol comps | M_r | major MS fragments |
|--|----------------|-------|--|
| 2-butyl-3,5-dipropylpyridine ^a | 12.1 | 219 | 149 (100), 162 (45), 177 (38), 204 (26), 176 (22), 190 (18), 150 (10), 41 (9), 183 (8) |
| 2,3-dihydro-2-butyl-3,5-dipropylpyridine ^a | 2.1 | 221 | 192 (100), 178 (51), 164 (50), 41 (31), 122 (25), 67 (22), 122 (20), 150 (20) |
| 3,5-dibutyl-1,2,4-trithiolane ^a (2 isomers) | 9.1 | 236 | 69 (100), 236 (35), 101 (34), 41 (32), 115 (32), 171 (28), 129 (20), 172 (18), 102 (18), 60 (16) |
| <i>N</i> -pentylidenepentenylamine ^a | 1.3 | 153 | 82 (100), 96 (50), 41 (44), 111 (42), 124 (39), 68 (27), 84 (25), 68 (23) |
| 2-propyl-2-heptenal | 1.0 | 154 | 125 (100), 154 (97), 41 (96), 55 (80), 81 (70), 69 (67), 43 (65), 111 (52), 97 (43) |
| 2-propyl-2-heptenoic acid | 1.5 | 170 | 127 (100), 85 (54), 82 (31), 43 (30), 41 (24), 96 (17), 170 (15) |

^a Reported for the first time.

Table II. Volatile Products Generated from the Reaction of Hexanal and Ammonium Sulfide

| product | % vol comps | M_r | major MS fragments |
|---|----------------|-------|---|
| 2-pentyl-3,5-dibutylpyridine ^a | 21.7 | 261 | 163 (100), 190 (32), 232 (24), 205 (14), 164 (12), 218 (10), 176 (10) |
| 2,3-dihydro-2-pentyl-3,5-dibutylpyridine ^a | 1.3 | 263 | 192 (100), 220 (92), 163 (44), 206 (41), 55 (36), 41 (30), 95 (28), 56 (26), 67 (24) |
| dihexyl sulfide ^a | 0.3 | 202 | 57 (100), 71 (68), 69 (66), 85 (58), 55 (51), 70 (46), 41 (46), 43 (42), 83 (42), 56 (40) |
| dihexyl disulfide ^a | 0.4 | 234 | 234 (100), 85 (92), 150 (85), 43 (82), 117 (42), 57 (33), 41 (30), 55 (25) |
| mercaptohexane | 5.0 | 118 | 118 (100), 56 (98), 69 (72), 55 (43), 41 (32), 84 (24), 43 (23), 42 (16), 47 (14), 61 (14) |
| <i>N</i> -hexylidenehexenylamine ^a | 0.4 | 181 | 82 (100), 110 (72), 138 (71), 112 (57), 125 (46), 41 (37), 55 (35), 56 (32), 68 (26), 98 (26) |
| hexanoic acid | 0.1 | 116 | 73 (100), 116 (67), 60 (42), 45 (24), 55 (21), 67 (21) |
| 2-butyl-2-octenal | 2.7 | 182 | 111 (100), 139 (86), 55 (77), 83 (72), 182 (70), 95 (62), 69 (60), 97 (55), 125 (54) |
| 2-butyl-2-octenoic acid | 8.4 | 198 | 141 (100), 57 (22), 85 (19), 142 (9), 41 (8), 198 (6) |

^a Reported for the first time.

Table III. Volatile Products Generated from the Reaction of Acetaldehyde, Pentanal, and Ammonium Sulfide

| product | % vol comps | M_r | major MS fragments |
|--|----------------|-------|---|
| 5,6-dihydro-2,4-dibutyl-6-methyl-4 <i>H</i> -1,3,5-dithiazine ^a | 19.8 | 247 | 112 (100), 86 (92), 113 (38), 247 (34), 70 (30), 98 (25), 145 (20) |
| 5,6-dihydro-4-butyl-2,6-dimethyl-4 <i>H</i> -1,3,5-dithiazine ^a | 11.6 | 205 | 86 (100), 112 (69), 205 (52), 70 (32), 44 (19), 113 (18), 60 (16), 98 (15), 145 (14) |
| 5,6-dihydro-2,4,6-tributyl-4 <i>H</i> -1,3,5-dithiazine ^a | 9.8 | 289 | 154 (100), 86 (25), 98 (20), 155 (18), 69 (10), 289 (9), 41 (8), 60 (5) |
| 5,6-dihydro-2-butyl-4,6-dimethyl-4 <i>H</i> -1,3,5-dithiazine ^a | 8.8 | 205 | 71 (100), 70 (75), 44 (65), 103 (64), 205 (54), 60 (22), 102 (18), 86 (15), 56 (14) |
| 5,6-dihydro-2,4,6-trimethyl-4 <i>H</i> -1,3,5-dithiazine | 8.5 | 163 | 44 (100), 163 (84), 71 (67), 70 (56), 103 (37), 60 (35), 59 (28), 56 (25) |
| 5,6-dihydro-4,6-dibutyl-2-methyl-4 <i>H</i> -1,3,5-dithiazine ^a | 6.6 | 247 | 154 (100), 86 (30), 98 (18), 247 (14), 155 (12), 112 (10), 69 (8), 60 (6) |
| 3,5-dibutyl-1,2,4-trithiolane (2 isomers) | 6.1 | 236 | 69 (100), 236 (61), 101 (38), 115 (34), 171 (33), 73 (33), 41 (24), 60 (20), 102 (20) |
| 3-methyl-5-butyl-1,2,4-trithiolane (2 isomers) | 2.8 | 194 | 69 (100), 194 (80), 101 (51), 129 (48), 92 (43), 60 (41), 41 (40), 87 (38), 59 (34), 130 (33) |
| 2,3-dihydro-2-butyl-3,5-dipropylpyridine ^a | 3.0 | 221 | 164 (100), 178 (98), 192 (97), 150 (43), 122 (34), 136 (26), 41 (17), 179 (16), 193 (16) |
| 2-butyl-3,5-dipropylpyridine ^a | 2.7 | 219 | 149 (100), 162 (60), 177 (42), 204 (28), 176 (26), 190 (22) |
| <i>N</i> -pentylidenepentenylamine ^a | 2.5 | 153 | 82 (100), 96 (52), 111 (46), 124 (42), 41 (38), 68 (28), 84 (25), 69 (24) |

^a Reported for the first time.

dimer, 1,4-dithiane-2,5-diol (McIntosh and Sieler, 1978), was purchased from Aldrich Chemical Co. (Milwaukee, WI). A 1:1 molar mixture of β -mercaptoacetaldehyde and aqueous 22% ammonium sulfide was heated in a sealed reaction vessel at 135 °C for 1 h. The reaction mixture was vacuum steam distilled, extracted, dried, and concentrated as previously described.

GC-MS Analysis. The concentrated extracts were analyzed by GC-MS using a Hewlett-Packard 5985 GC-MS system. The GC was fitted with a 30 m \times 0.25 mm i.d., 0.25- μ m film, DB-1 fused silica capillary column (J&W Scientific, Inc., Rancho Cordova, CA). The column oven temperatures was held at 40 °C for 2 min and then programmed to 250 °C at 4 °C/min. Mass spectra were obtained at 70 eV and a source temperature of 200 °C. The percent concentrations of volatile compounds identified were calculated from the total ion chromatogram.

RESULTS AND DISCUSSION

Tables I-VI summarize the reactions that we examined. All of the reactants are expected to be present naturally during the frying of chicken or potatoes. Acetaldehyde,

β -mercaptoacetaldehyde, pentanal, and isopentanal are Strecker aldehydes. Hexanal is a major component of lipid decomposition. Hydrogen sulfide and ammonia are derived from ammonium sulfide during the reaction process. Hydrogen sulfide is formed from the degradation of sulfur-containing amino acids in foods. Ammonia can be provided by any amino acid.

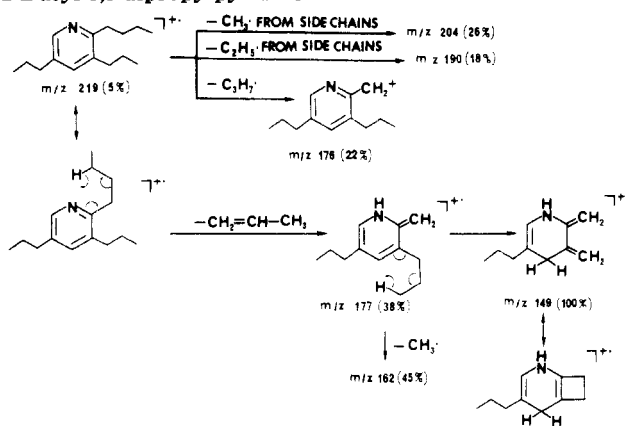
The structure assignment of the reaction products was solely based on the interpretation of mass spectral data. Therefore, all the novel compounds listed are only considered as tentative identification. Tables I and II list the mass spectral fragmentations and percent concentrations of volatile compounds identified in the reaction of pentanal/ammonium sulfide and hexanal/ammonium sulfide, respectively. The expected 2,3,5-trialkylpyridines were the most abundant compounds identified in each reaction. The mass spectrometric fragmentation of 2,3,5-trialkylpyridine identified in our reactions closely resembled that of 2-isobutyl-3,5-diisopropylpyridine reported by Shu et al. (1985). The obvious discrepancy of mass spectra between our trialkylpyridine and 2-isobutyl-3,5-diisopropylpyridine reported by Shu et al. (1985) is the m/z

Table IV. Volatile Products Generated from the Reaction of Acetaldehyde, Isopentanal, and Ammonium Sulfide

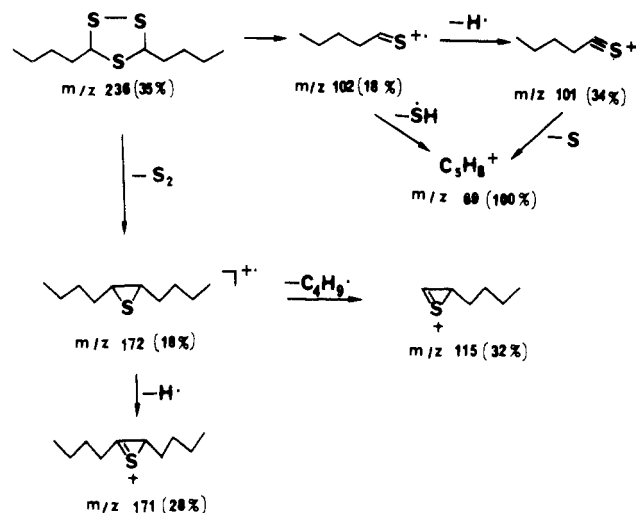
| product | % vol compds | M_r | major MS fragments |
|---|--------------|-------|--|
| 5,6-dihydro-2,4-diisobutyl-6-methyl-4H-1,3,5-dithiazine ^a | 17.0 | 247 | 86 (100), 112 (85), 70 (80), 113 (42), 247 (35), 44 (35), 69 (22), 145 (20) |
| 5,6-dihydro-2,4,6-trimethyl-4H-1,3,5-dithiazine | 6.5 | 163 | 44 (100), 163 (64), 71 (47), 70 (42), 60 (32), 103 (26), 43 (24) |
| 5,6-dihydro-4-isobutyl-2,6-dimethyl-1,3,5-dithiazine ^a | 5.6 | 205 | 86 (100), 70 (85), 112 (67), 205 (54), 44 (52), 69 (22), 43 (21), 113 (20), 145 (18) |
| 5,6-dihydro-2-isobutyl-4,6-dimethyl-1,3,5-dithiazine ^a | 4.3 | 205 | 44 (100), 71 (69), 70 (62), 205 (38), 103 (35), 69 (63), 86 (17), 56 (17), 43 (16) |
| 3,5-diisobutyl-1,2,4-trithiolane ^a (2 isomers) | 0.8 | 236 | 69 (100), 41 (66), 43 (55), 236 (48), 112 (40), 70 (34), 101 (31) |
| 3-methyl-N-(3-methylbutylidene) butenylamine ^a (2 isomers) | 2.2 | 153 | 96 (100), 82 (49), 110 (46), 41 (45), 111 (36), 54 (35), 138 (34), 43 (26) |
| 3-methyl-N-methylenebutenylamine ^a (2 isomers) | 0.4 | 111 | 96 (100), 55 (42), 41 (32), 68 (24), 111 (24), 42 (21), 81 (20), 39 (20), 40 (19) |

^a Reported for the first time.**Table V. Volatile Products Generated from the Reaction of Acetaldehyde, Hexanal, and Ammonium Sulfide**

| product | % vol compds | M_r | major MS fragments |
|--|--------------|-------|---|
| 2-pentyl-3,5-dibutylpyridine ^a | 15.6 | 261 | 163 (100), 190 (28), 232 (18), 164 (12), 176 (12), 41 (10), 120 (10), 205 (8), 218 (8) |
| 5,6-dihydro-2,4-dipentyl-6-methyl-4H-1,3,5-dithiazine ^a | 14.0 | 275 | 126 (100), 100 (48), 70 (24), 44 (20), 127 (20), 112 (15), 60 (12) |
| 5,6-dihydro-2-pentyl-4,6-dimethyl-4H-1,3,5-dithiazine ^a | 13.8 | 219 | 44 (100), 71 (78), 70 (63), 103 (38), 126 (22), 219 (20), 60 (20), 43 (17), 41 (15) |
| 5,6-dihydro-4-pentyl-2,6-dimethyl-4H-1,3,5-dithiazine ^a | 13.3 | 219 | 126 (100), 100 (74), 44 (41), 70 (40), 219 (26), 60 (18), 127 (16), 41 (15), 59 (14) |
| 5,6-dihydro-2,4,6-trimethyl-4H-1,3,5-dithiazine ^a | 11.4 | 163 | 44 (100), 71 (39), 163 (37), 70 (32), 60 (22), 59 (18), 103 (15), 51 (14) |
| 5,6-dihydro-4,6-dipentyl-2-methyl-4H-1,3,5-dithiazine ^a | 4.0 | 275 | 182 (100), 100 (40), 112 (32), 41 (18), 55 (16), 60 (15), 43 (15), 183 (14) |
| 3-methyl-5-pentyl-1,2,4-trithiolane | 1.6 | 208 | 115 (100), 55 (97), 41 (86), 208 (83), 82 (72), 87 (66), 60 (62), 59 (62), 92 (56), 83 (54), 143 (53) |
| mercaptohexane | 0.5 | 118 | 56 (100), 118 (52), 41 (50), 43 (50), 69 (48), 55 (45), 42 (42) |

^a Reported for the first time.**Scheme I. Proposed Fragmentation of 2-Butyl-3,5-dipropylpyridine**

43 of Shu and the m/z 193 ($M - 43$) of our work. This is probably due to the fact that the isopropyl group more easily bears the positive charge than the *n*-propyl group. Scheme I summarizes the fragmentation of 2-butyl-3,5-dipropylpyridine. The base peak at m/z 149 probably results from two successive MacLafferty rearrangements of two higher alkyl side chains. Chichibabin (1924) reported the synthesis of 2,3,5-trialkylpyridine from aldehyde and ammonia. Shu et al. (1985) proposed a mechanism for the Chichibabin formation of 2,3,5-trialkylpyridine. Hexanal is the most abundant aldehyde in the flavor of fried foods and is formed primarily from the frying fat through thermal and oxidative reactions. It is therefore reasonable to expect the presence of 2-pentyl-3,5-dibutylpyridine, the Chichibabin pyridine of hexanal, in fried food flavor. Mass spectral data from the reaction of hexanal/ammonium sulfide allowed us to identify this compound in french-fried potato flavor (Carlin et al., 1985).

Scheme II. Fragmentation of 3,5-Dibutyl-1,2,4-trithiolane

Another important class of compounds identified in the reactions of aldehydes with ammonium sulfide is the 1,2,4-trithiolanes. They have received increased attention since the identification of diastereomeric 3,5-dimethyl-1,2,4-trithiolane in the volatiles of boiled beef (Chang et al., 1968). The parent 1,2,4-trithiolane is a component of mushroom (Chen, et al., 1984) and red algae (Ohloff and Flament, 1978). In addition to 3,5-dimethyl-1,2,4-trithiolane, Kubota et al. (1980) identified 3-methyl-5-ethyl-1,2,4-trithiolane and 3,5-diethyl-1,2,4-trithiolane in both *cis* and *trans* forms in boiled Antarctic Gulls. Both compounds were described as garlicky. Flament et al. (1978) reported the identification of 3-methyl-5-ethyl-1,2,4-trithiolane and 3-methyl-5-isopropyl-1,2,4-trithiolane in a commercial beef extract. The *cis* and *trans* forms of

Table VI. Volatile Products Generated from the Reaction of β -Mercaptoacetaldehyde and Ammonium Sulfide

| product | % vol compds | M_r | major MS fragments |
|--|--------------|-------|--|
| 5,6-dihydro-2,4,6-trimethyl-4 <i>H</i> -1,3,5-dithiazine (3 isomers) | 59.5 | 163 | 44 (100), 60 (50), 59 (45), 28 (43), 45 (35), 70 (30), 43 (25), 71 (24), 27 (24), 163 (22) |
| 5,6-dihydro-2,4-dimethyl-6-ethyl-4 <i>H</i> -1,3,5-dithiazine ^a | 0.7 | 177 | 58 (100), 59 (84), 44 (76), 60 (76), 45 (75), 41 (73), 27 (51), 58 (40), 70 (35) |
| 5,6-dihydro-2-ethyl-4,6-dimethyl-4 <i>H</i> -1,3,5-dithiazine ^a | 0.5 | 177 | 44 (100), 45 (67), 41 (59), 70 (48), 59 (41), 74 (39), 71 (37), 42 (34), 27 (33) |
| 3,5-dimethyl-1,2,4-trithiolane (2 isomers) | 1.3 | 155 | 59 (100), 152 (75), 60 (67), 45 (58), 92 (52), 88 (48), 64 (47) |
| 4-methyl-5-ethylthiazole | 0.4 | 127 | 112 (100), 127 (60), 85 (59), 45 (56), 126 (43) |
| 2-methylthiazole | 0.3 | 99 | 58 (100), 99 (58), 57 (17), 45 (9), 59 (9) |
| 2,4,5-trimethylthiazole | 0.1 | 127 | 71 (100), 127 (84), 86 (65), 42 (36), 59 (28), 85 (27) |
| 2,4,5-trimethyl-3-thiazoline | 0.1 | 129 | 88 (100), 42 (98), 69 (82), 55 (61), 68 (56), 129 (51), 45 (46), 27 (45) |
| diethyl trisulfide | 1.2 | 154 | 61 (100), 29 (95), 154 (93), 27 (70), 59 (36), 64 (31), 45 (28), 93 (27) |
| diethyl disulfide | 0.1 | 122 | 29 (100), 66 (98), 122 (96), 94 (70), 45 (32) |
| 4,7-dimethyl-1,2,3,5,6-pentathiacycloheptane | 0.7 | 216 | 59 (100), 60 (89), 45 (71), 92 (62), 156 (45), 58 (38), 64 (34), 27 (31) |
| 4,6-dimethyl-1,2,3,5-tetrathiacyclohexane (2 isomers) | 0.4 | 184 | 59 (100), 60 (58), 184 (39), 124 (26), 45 (25), 64 (19) |
| ethyl 1-(ethylthio)ethyl disulfide | 0.1 | 182 | 89 (100), 61 (69), 59 (50), 45 (40), 27 (39), 58 (34), 60 (34) |
| 5-methyl-2-thiophenecarboxaldehyde | 0.3 | 126 | 125 (100), 126 (99), 97 (76), 45 (44), 53 (39) |

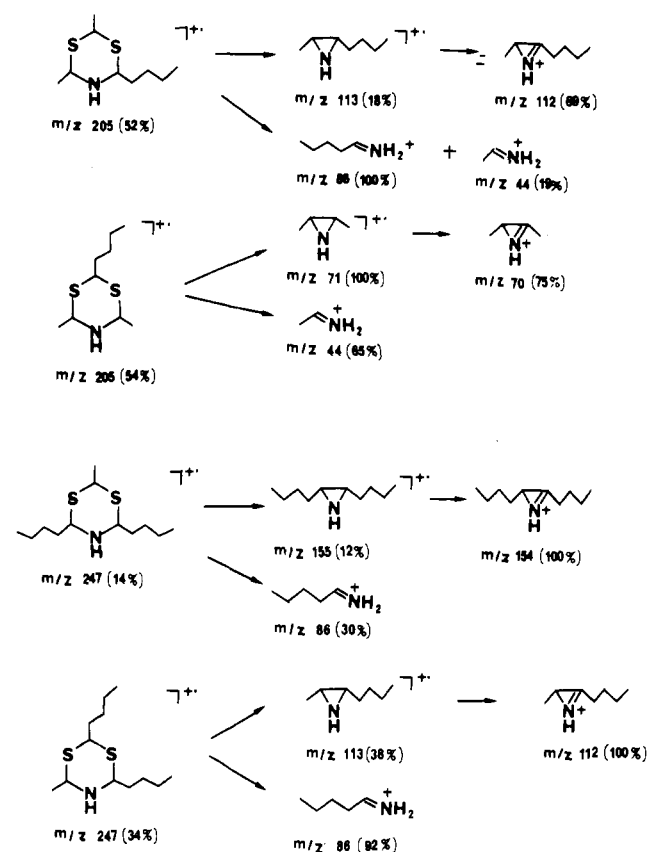
^a Reported for the first time.

3,5-dibutyl-1,2,4-trithiolane were identified in the reaction of pentanal/ammonium sulfide and constituted 9.1% of the volatile compounds. Mass spectral fragmentation of 3,5-dibutyl-1,2,4-trithiolane is summarized in Scheme II. The main feature of the fragmentation is the successive loss of the $C_5H_{10}S_2$ fragment and the $HS\cdot$ radical, giving the base peak at m/z 69. However, the expected 3,5-dipentyl-1,2,4-trithiolanes were not identified in the reaction of hexanal/ammonium sulfide. This may be due to low volatility of these compounds.

Tables III-V list the mass spectral fragmentation and percent concentrations of volatile compounds identified in the reaction of mixed aldehydes (acetaldehyde/pentanal, acetaldehyde/isopentanal, acetaldehyde/hexanal) with ammonium sulfide. Mass spectral data from the reaction of acetaldehyde/pentanal/ammonium sulfide and acetaldehyde/hexanal/ammonium sulfide allowed us to identify the predicted trithiolane products, 3-methyl-5-butyl-1,2,4-trithiolane and 3-methyl-5-pentyl-1,2,4-trithiolane in fried chicken flavor (Ho and Chang, 1985).

Table VI lists the mass spectral fragmentation and percent concentrations of volatile compounds identified in the reaction of β -mercaptoacetaldehyde/ammonium sulfide. Three stereoisomers of 5,6-dihydro-2,4,6-trimethyl-4*H*-1,3,5-dithiazine, also known as thialdine, were identified. Together they constituted 59.5% of the volatile compounds generated. The exact stereochemistry of the isomers has not been determined. It is interesting to note that the formation of one of the three isomers (51.0%) is so highly favored over the other two (4.5% and 4.0%). Thialdine has been previously identified in the volatiles of pressure-cooked meat (Wilson et al., 1973) and fried chicken (Tang et al., 1983).

The 5,6-dihydro-4*H*-1,3,5-dithiazines were an important class of compounds identified in the reactions of mixed aldehydes with ammonium sulfide and β -mercaptoacetaldehyde/ammonium sulfide. A total of 13 of these compounds were identified, and they existed at significant concentrations. The mass spectral fragmentations of 5,6-dihydro-4*H*-1,3,5-dithiazines provided abundant information for the assignment of structures and differentiation between isomers. Scheme III presents the main fragmentations of two isomers of 5,6-dihydro-4*H*-1,3,5-dithiazines with one butyl and two methyl substituents and two isomers of 5,6-dihydro-4*H*-1,3,5-dithiazines with one methyl and two butyl substituents. Both sets of isomers

Scheme III. Fragmentation of 5,6-Dihydro-4*H*-1,3,5-dithiazines

can be distinguished because the 2-methyl-substituted isomers undergo the expulsion of a fragment of $C_2H_4S_2$ from the molecular ions, while the 2-butyl-substituted isomers give the fragment ions with the loss of $C_5H_{10}S_2$ elements. With the exception of thialdine, none of the 5,6-dihydro-4*H*-1,3,5-dithiazines generated from the reaction studies have been identified in food flavors. These compounds are known to be potent flavoring agents. Several of the dithiazines identified in our work have green and vegetable-like odors (Pickenhagen, 1984).

Besides 1,3,5-dithiazines, the two isomeric 3,5-dimethyl-1,2,4-trithiolanes, thiazoles, sulfides, a thiophene, and three miscellaneous compounds were identified in the

reaction of β -mercaptoacetaldehyde/ammonium sulfide. Ethyl 1-(ethylthio)ethyl disulfide was identified and has been reported in the volatiles generated from thermal decomposition of cystine in water (Shu et al., 1985).

Thiazoles were among the most important compounds identified in fried chicken and french-fried potato flavors. A total of 16 were identified in fried chicken flavor (Tang et al., 1983) and 50 in french-fried potato flavor (Carlin, 1983). Thiazoles possess potent sensory characteristics. Several of the thiazoles identified in our studies have odors that are reminiscent of fried food and could be important contributors to that aspect of fried chicken or french-fried potato flavor. Takken et al. (1976) proposed a mechanism for the formation of thiazoles involving aldehydes, hydrogen sulfide, and ammonia.

Reaction experiments between selected aldehydes and ammonium sulfide allowed us to identify 3-methyl-5-butyl-1,2,4-trithiolane and 3-methyl-5-pentyl-1,2,4-trithiolane in fried chicken flavor and 2-pentyl-3,5-dibutylpyridine in french-fried potato flavor. Other compounds identified such as the 1,3,5-dithiazines have potent sensory characteristics but have not yet been detected in food. The mass spectral data are listed for all compounds identified in the hope that they will assist researchers in the characterization of food flavors.

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Lipid Content and Fatty Acid Composition of Indica and Japonica Types of Nonglutinous Brown Rice

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The lipid content and fatty acid composition of Indica and Japonica types of nonglutinous brown rice were investigated on 20 cultivars each of both types. The Indica type, as compared with the Japonica type, gave significantly higher palmitic acid, stearic acid, and arachidic acid contents and lower lipid content and linoleic acid, eicosenoic acid, and lignoceric acid contents. As to the relationship between fatty acid contents, there were the highest and negative correlations between oleic acid and linoleic acid in both types. The scatter diagram between both fatty acids could be divided into Indica and Japonica types.

In previous work, it was shown that the lipid content and fatty acid composition of brown rice were influenced by nonglutinous and glutinous types (Taira et al., 1981; Taira and Hiraiwa, 1982), cropping year (Taira et al., 1979a), and cropping season (Taira et al., 1979b). Rice can be classified into at least two groups, Indica type (*Oryza sativa* L. subsp. *indica* Kato) and Japonica type (*O. sativa* L. subsp. *japonica* Kato). As to the difference of chemical composition between both types of rice, Indica type, as

compared with Japonica type, is higher in amylose content of nonglutinous starch (Hsieh et al., 1964; Juliano et al., 1964; Horiuchi and Tani, 1966). Little information, however, is available on the difference of the lipid content and fatty acid composition between both types of rice. Therefore, investigations were undertaken to study the lipid content and fatty acid composition of nonglutinous brown rice using Taiwanese cultivars of Indica and Japonica Types.

METHODS AND MATERIALS

Mature grains of 20 nonglutinous cultivars each of Indica and Japonica types were collected from a field experiment conducted as second crop by the Chiayi Agricultural Experiment Station, Taiwan, in 1980. The transplanting time

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