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Positive Identification of New Alkyloxazoles, Alkylthiazoles, and Piperidine in Roasted Peanut Flavor

Previous work provided evidence of the occurrence of new alkyloxazoles, alkythiazoles, and 2-(2-aminoethyl)piperidine in the volatiles of freshly roasted peanuts. Here the synthesis and mass spectral data of these compounds are reported.

Roasted peanuts possess a unique and widely enjoyed flavor. There are more than 350 volatile compounds identified in roasted peanuts (Buckholz and Daun, 1981). Recently, we reported the identification of 131 compounds in the volatile flavor constituents of freshly roasted peanuts (Ho et al., 1982).

Thiazoles and oxazoles have recently been recognized as important flavor components in food. Walradt et al. (1971) identified thiazole, 4-methylthiazole, and benzothiazole in the volatiles of roasted peanuts. Buckholz and Daun (1981) reported the identification of 2,4-dimethyl-3-thiazoline in roasted peanut flavor and found that it added deep roasted notes and contributed to the nut skin character. We reported the identification of eight thiazoles, seven oxazoles, and three oxazolines in roasted peanut flavor (Lee et al., 1981). However, due to the lack of reference mass spectral data, several alkylthiazoles, alkyloxazoles, and a piperidine derivative were only tentatively identified (Lee, 1980).

In the present paper, we report the synthesis and mass spectral data of six oxazoles, seven thiazoles, and 2-(2-aminoethyl)piperidine.

EXPERIMENTAL SECTION

Synthesis of α -Bromo Ketones. α -Bromo ketones were synthesized by the method described by Catch et al. (1948), which involves essentially direct bromination of the appropriate ketone. With unsymmetrical ketones, two bromo ketones are formed. In all cases, the mixture of the two bromides was taken through the oxazole synthesis and the two isomeric oxazoles were separated by GC.

Synthesis of Alkyloxazoles. These were all synthesized by the method of Theilig (1953). One equivalent of α -bromo ketone was allowed to react with 2 equiv of amide. Yields were all generally quite satisfactory at about 50%. The distilled products were purified by GC.

Synthesis of Alkylthiazoles. Alkylthiazoles were synthesized by the method of Kurkijy and Brown (1952) by the addition of the α -bromo ketone to the preformed thioamide. Yields were all quite satisfactory at about 50%. The steam distilled products were then purified by GC.

Synthesis of 2-(2-Aminoethyl)piperidine. To 5 g of 2-(2-aminoethyl)pyridine (Aldrich Chemical Co.) in 100 mL of diethyl ether dry hydrogen chloride gas was intro-

Table I. Mass Spectral Data of New Compounds Identified in Roasted Peanut Flavor by Comparison with Synthetic Authentic Compounds

compound identified	MS data, ^a <i>m/z</i> (rel intensity)
2-methyl-4-butyloxazole	25 (60), 28 (34), 41 (19), 42 (38), 55 (5), 56 (10), 68 (51), 69 (9), 82 (7), 83 (3), 96 (20), 97 (100), 110 (15), 111 (3), 124 (10), 125 (2), 138 (2), 139 (11); M = 139
2,4-dimethyl-5-propyloxazole	26 (4), 27 (16), 42 (34), 43 (23), 55 (4), 56 (2), 68 (13), 69 (4), 82 (2), 83 (1), 96 (1), 97 (1), 110 (100), 111 (8), 124 (1), 139 (14), 140 (1); M = 139
2-isopropyl-4,5-dimethyloxazole	27 (36), 28 (20), 42 (50), 43 (59), 54 (17), 55 (46), 69 (6), 70 (22), 80 (4), 82 (4), 96 (39), 97 (3), 110 (2), 111 (1), 124 (100), 125 (10), 138 (7), 139 (31); M = 139
2-methyl-4-propyl-5-ethyloxazole	27 (49), 29 (100), 41 (56), 42 (40), 55 (32), 57 (50), 67 (5), 68 (5), 83 (56), 84 (4), 96 (12), 97 (4), 110 (10), 111 (2), 124 (88), 125 (44), 138 (18), 139 (2), 152 (3), 153 (19); M = 153
2-isopropyl-4-ethyl-5-methyloxazole	27 (43), 28 (60), 41 (42), 43 (100), 55 (18), 56 (21), 69 (44), 70 (10), 83 (2), 84 (8), 96 (37), 97 (3), 110 (30), 111 (3), 124 (4), 138 (84), 139 (10), 152 (5), 153 (26); M = 153
2,4-diethyl-5-propyloxazole	27 (34), 29 (50), 39 (28), 41 (39), 55 (38), 56 (30), 69 (8), 71 (4), 82 (5), 83 (13), 96 (3), 97 (4), 110 (3), 111 (2), 124 (14), 125 (2), 138 (100), 139 (11), 152 (5), 153 (1), 167 (15), 168 (2); M = 167
2-methyl-4-ethyl-5-propylthiazole	27 (4), 29 (4), 41 (8), 45 (8), 55 (6), 59 (14), 65 (9), 71 (5), 79 (3), 85 (5), 97 (3), 99 (19), 112 (3), 113 (3), 126 (6), 127 (6), 140 (100), 141 (18), 154 (18), 155 (3), 169 (14), 170 (5); M = 169
2-isopropyl-4-ethyl-5-methylthiazole	27 (40), 29 (30), 39 (44), 41 (50), 56 (19), 59 (62), 67 (18), 71 (10), 85 (60), 86 (5), 97 (2), 99 (12), 110 (20), 111 (2), 126 (4), 127 (11), 139 (7), 141 (4), 154 (100), 155 (13), 168 (19), 169 (50); M = 169
2-isopropyl-4-propylthiazole	27 (50), 29 (19), 39 (34), 45 (54), 53 (8), 55 (10), 70 (18), 71 (55), 85 (13), 87 (4), 97 (4), 99 (9), 110 (2), 112 (3), 125 (5), 126 (10), 140 (16), 141 (100), 154 (43), 155 (5), 168 (14), 169 (14); M = 169
2,4-diethyl-5-propylthiazole	27 (35), 29 (30), 41 (45), 45 (47), 55 (19), 59 (34), 65 (28), 71 (14), 79 (10), 85 (11), 95 (6), 99 (35), 111 (4), 113 (4), 126 (4), 128 (3), 139 (3), 140 (7), 154 (100), 155 (41), 168 (25), 169 (3), 182 (7), 183 (34); M = 183
2,5-diethyl-4-propylthiazole	27 (9), 29 (10), 39 (14), 41 (15), 45 (20), 55 (8), 59 (15), 65 (15), 71 (11), 77 (5), 85 (6), 97 (5), 99 (32), 112 (1), 113 (2), 126 (3), 127 (4), 140 (19), 141 (3), 154 (57), 155 (100), 168 (34), 169 (4), 182 (14), 183 (44); M = 183
2,5-dipropyl-4-methylthiazole	27 (17), 29 (11), 41 (21), 45 (32), 53 (11), 59 (14), 71 (24), 72 (7), 78 (9), 85 (24), 97 (3), 99 (5), 112 (29), 113 (16), 125 (5), 126 (23), 140 (7), 141 (72), 154 (77), 155 (100), 168 (26), 169 (3), 182 (8), 183 (25); M = 183
2-butyl-4-methyl-5-ethylthiazole	27 (23), 28 (20), 41 (24), 45 (36), 53 (6), 55 (6), 67 (10), 73 (43), 84 (6), 85 (8), 97 (3), 99 (5), 112 (14), 113 (9), 125 (4), 126 (2), 141 (100), 142 (11), 154 (23), 155 (41), 168 (14), 169 (2), 182 (6), 183 (5); M = 183
4-methyl-5-(2-hydroxyethyl)thiazole ^b	27 (11), 28 (1), 39 (9), 45 (38), 58 (7), 59 (10), 71 (9), 72 (6), 85 (41), 86 (6), 97 (2), 98 (1), 112 (100), 113 (49), 124 (1), 125 (2), 143 (51), 144 (4); M = 143
2-(2-aminoethyl)piperidine	28 (18), 30 (57), 42 (11), 43 (13), 55 (9), 56 (38), 70 (7), 71 (4), 84 (100), 85 (7), 93 (4), 98 (8), 110 (8), 111 (23), 127 (1), 128 (1); M = 128

^a The two most intense ions every 14 mass units above 20 are listed. ^b Matches well with the spectrum reported (Jennings and Shibamoto, 1980).

duced into an ether solution. The pyridine salt formed was separated by filtration. A total of 7 g of 2-(2-aminoethyl)pyridine hydrochloride was dissolved in 300 mL of absolute ethanol and 12 mL of water and placed in the Parr apparatus. Palladium on charcoal (1.5 g of 10% catalyst) was added, and the system was briefly evacuated. Hydrogen was introduced to a pressure of 450 psi and the system was stirred at 65 °C for 5 h. At the conclusion of the hydrogenation, the catalyst was removed by filtration through Celite, and the filtrate was concentrated by using a rotary evaporator. The residue was alkalinized with 50% sodium hydroxide solution and extracted with diethyl ether. The ether solution was dried over anhydrous sodium sulfate. After removal of the ether, vacuum distillation gave 215 g of colorless liquid, bp 77–79 °C/5 mmHg.

Mass Spectra. 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 80–100-mesh Chromosorb W. The ionization voltage was 70 eV.

RESULTS AND DISCUSSION

Six alkyloxazoles and seven alkylthiazoles tentatively identified in the volatiles of freshly roasted Florida Runner peanuts were synthesized by the reaction of corresponding α -bromo ketone with amide (Theilig, 1953) or thioamide (Kurkijy and Brown, 1952). The mass spectral data of synthesized alkyloxazoles and alkylthiazoles are tabulated in Table I. The structures of synthesized alkyloxazoles and alkylthiazoles can be confirmed by their mass spectral fragmentation patterns (Bowie et al., 1968; Ho and Jin, 1983; Buttery et al., 1973). The mass spectra of the isolated compounds matched well with those of the synthetic compounds.

Alkyloxazoles are mainly associated with a green sweet, earthy, and vegetable-like odor impression. The sensory

properties of some 4,5-dialkylloxazoles had been studied (Ho and Tuorto, 1981). The 2,4-diethyl-5-propyloxazole synthesized had a strong sweet and fatty aroma. Today there is no longer any doubt about the importance of thiazoles as constituents of food aromas (Ohloff and Flament, 1978). According to Pittet and Hruza (1974), the odor of alkylthiazoles had generally been described as green, nutty, and vegetable-like. This holds true for the alkylthiazoles synthesized in this study. 2-Isopropyl-4-ethyl-5-methylthiazole was described as having a raw sweet potato-like aroma, and 2,5-diethyl-4-propylthiazole had a pleasant fruity, green, and mango-like odor impression.

A novel compound, 2-(2-aminoethyl)piperidine, was identified by comparing its mass spectrum with that of the authentic synthetic compound. 2-(2-Aminoethyl)piperidine was synthesized by the hydrogenation of 2-(2-aminoethyl)pyridine. Table I lists the mass spectral data of synthetic 2-(2-aminoethyl)piperidine, which matched well with those of the isolated compound. The base peak at m/z 84 is due to the loss of the $-\text{CH}_2\text{CH}_2\text{NH}_2$ radical from the molecular ion. The large ion at m/z 30 suggests the presence of a CH_2NH_2^+ ion. The broad absorption at 3400 cm^{-1} in the infrared spectrum of 2-(2-aminoethyl)piperidine also supports the presence of amino group. The 2-(2-aminoethyl)piperidine synthesized had a weak nutty aroma.

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Registry No. 2-Methyl-4-butyloxazole, 84027-87-2; 2,4-dimethyl-5-propyloxazole, 84027-86-1; 2-isopropyl-4,5-dimethyl-oxazole, 19519-45-0; 2-methyl-4-propyl-5-ethyloxazole, 84027-92-9; 2-isopropyl-4-ethyl-5-methyloxazole, 84027-96-3; 2,4-diethyl-5-propyloxazole, 77311-03-6; 2-methyl-4-ethyl-5-propylthiazole, 41981-75-3; 2-isopropyl-4-ethyl-5-methylthiazole, 87116-68-5; 2-isopropyl-4-propylthiazole, 87116-69-6; 2,4-diethyl-5-propylthiazole, 87116-70-9; 2,5-diethyl-4-propylthiazole, 4276-68-0; 2,5-dipropyl-4-methylthiazole, 87116-71-0; 2-butyl-4-methyl-5-ethylthiazole, 86290-20-2; 4-methyl-5-(2-hydroxyethyl)thiazole, 137-00-8; 2-(2-aminoethyl)piperidine, 15932-66-8; 2-(2-aminoethyl)pyridine, 2706-56-1.

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Fermented Cassava: Odor Active Components

Cassava (*Manihot Esculanta* Crantz), a root crop, occupies a unique position as a staple food crop in the tropics. In Nigeria, the tubers are processed to garri and also fermented in cold water and sieved to give a fermented mass used to prepare cassava fufu. The fermentation of cassava tubers in cold water usually imparts an objectionable odor to the fermented mass and the cooked fufu. The compounds responsible for this odor have been isolated from the acidic fraction of fermentation liquor and analyzed by combined gas chromatography and mass spectrometry. The acids identified are butanoic acid, propanoic acid, and acetic acid, butanoic acid being responsible for the objectionable odor.

Cassava, though low in useful protein content, plays an vital role as one of the major sources of carbohydrate to 200-300 million people in the tropics (Nestle, 1973). Although cassava-based food products (such as garri and fufu in Nigeria) are considered to be of inferior food value, it is significant to note that in areas where cassava is ex-

tensively grown, even by traditional methods, severe famine seldom occurs, because of its great reliability (Cock and Howler, 1978). In Nigeria at least the government has realized this and is running a program to boost tuber production to at least 10 million metric tons annually. The deficiency in protein of cassava-based food products has