

properties of some 4,5-dialkyloxazoles 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  $\text{CH}_2\text{NH}_2^+$  ion. The broad absorption at  $3400\text{ cm}^{-1}$  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 Howeler, 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

Table I. GC-MS Data for Cassava Acidic Fraction

peak	retention time, min	M <sup>+</sup>	mass spectral data, m/z (rel intensity)	identification	area, %
1	8.2	60 (78)	45 (90), 43 (100), 42 (13), 29 (11)	acetic acid	6
2	10.1	74 (100)	73 (62), 57 (30), 45 (58), 29 (100), 28 (88), 27 (78)	propanoic acid	11
3	12.0	88 (3)	73 (41), 60 (100), 43 (21), 42 (21), 41 (30), 27 (38)	butanoic acid	83

not in any way had many adverse comments from its consumers as has the objectionable odor of tuber fermentation, which has been overlooked by investigators in the field of cassava and its food products. It is observed that the obnoxious odor associated with aqueous tuber fermentation is independent of the variety of the cassava and the odor has not only reduced the proportion of potential users but also induced a situation where many would not publicly admit eating fufu and also made it derogatory for fufu to be served in public as is common with garri.

The aim of this work is to identify the compound(s) responsible for the obnoxious odor induced by aqueous fermentation and the possible origin.

#### MATERIALS AND METHODS

**Fermentation and Extraction.** Cassava tubers of the bitter variety (which is the commonest cultivated type) were fermented in line with the traditional method. Peeled, cut, and washed tubers were submerged in cold water in plastic containers and left to stand for 4 days during which fermentation was complete as indicated by the presence of obnoxious odor and softening of the tubers.

The fermentation liquor was decanted and extracted with redistilled diethyl ether. The ether extract was concentrated to 500 cm<sup>3</sup> and separated into acidic, basic, and neutral components by countercurrent solvent extraction according to Alders (1955).

**Origin of the Acids.** Fresh, peeled, and washed tubers were grated, dried, and extracted with redistilled petroleum ether, bp 60–80 °C. The oil recovered after distilling off the spirit was portioned into two and one part hydrolyzed with molar sulfuric acid (1 cm<sup>3</sup> of the oil to 20 cm<sup>3</sup> of the acid), and the other part hydrolyzed with 2 M sodium hydroxide in quantities similar to that of acid hydrolysis.

**GC-MS Analysis.** The free acid fraction was separately analyzed by a combined gas chromatography-mass spectrometry (GC-MS) technique, using a Pye Model 104 gas chromatograph (GC), equipped with a flame ionization detector, coupled through an A.E.I. silicone rubber membrane separator to an updated fast scanning A.E.I. Model MS9 mass spectrometer (MS). The M 5 G was fitted with a mass spectrometry services replacement console with fast scanning capability and a V.G. Model 2015 data handling system. The ionization potential of the ionizing electrons was 70 eV.

The chromatographic column used was a 2.5 m × 4 mm i.d. glass column coated with 5% Carbowax 20M-TPA on 100–120-mesh Chromosorb G-AW-DMCS. The oven temperature was programmed from 60 to 150 °C at 3 °C/min, the temperature of the injector was 200 °C and the detector was at 250 °C, and the helium flow rate was 40 cm<sup>3</sup>/min.

#### RESULTS AND DISCUSSION

The separation of the liquor extract yielded only an acidic and a neutral product. The neutral extract was oily, possessing no obnoxious odor, but the acid fraction by olfactory evaluation possessed the obnoxious odor.

The analysis of the acid fraction revealed that only acetic, propanoic, and butanoic acids were present and in that order of increasing occurrence (see Table I). The identities of these compounds were confirmed by comparison with authentic samples and by comparison with the "Eight Peak Index of Mass Spectra".

Comparison of 1% v/v butanoic acid in water with the fermentation liquor showed butanoic acid to be primarily responsible for the fermentation odor.

The acid or base hydrolysis of the oil extracted from unfermented tuber did not produce a hydrolysate with the objectionable odor nor any volatile acid. This then showed that the acids from aqueous fermentation were not present in the combined form (as esters) in cassava tuber; instead they are produced during fermentation. In support of this is the report by Finar (1970) and others that C<sub>2</sub> to C<sub>6</sub> acids are common products of carbohydrate fermentation by *Bacillus butrycus*.

**Registry No.** Butanoic acid, 107-92-6; propanoic acid, 79-09-4; acetic acid, 64-19-7.

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