Earthy Aroma of Potatoes

2-Methoxy-3-isopropylpyrazine has been characterized with some certainty in the basic fraction of the vacuum steam volatile oil of potatoes using the direct combination of capillary gas-liquid chromatography and mass spectrometry. In the authors' opinion, this compound is a major contributor to the earthy aroma of potatoes.

One of the most characteristic features of potatoes is their earthy odor. Over 10 years ago we isolated a gas-liquid chromatographic (glc) fraction that possessed an earthy odor from the steam volatile oil of potatoes, but at that time we could not characterize the compound responsible for the odor because of its minute amount. More recently (Buttery *et al.*, 1970) we suspected that this compound was an alkylmethoxypyrazine, and tentative evidence indicated that it was 2-ethyl-3-methoxypyrazine. However, the compound occurs in potatoes at such a low concentration that the amount isolated was still too small to characterize positively. This communication reports the results of studies in which larger amounts of this compound were isolated and characterized with some degree of certainty to be 2-methoxy-3-isopropylpyrazine.

EXPERIMENTAL SECTION

Isolation of Steam Volatile Basic Fraction. Oregon Russet Burbank potatoes (45 kg) were cut into cubes (1.3-cm sides) and treated in a Likens-Nickerson head-equipped vacuum steam distillation continuous extraction apparatus (90 l.) of a type previously described (Buttery *et al.*, 1971). The potato cubes were covered with water for the isolation. Hexane (150 ml) was used as the extracting solvent. Pressure was kept at 80–100 mm, with the product boiling at 45–50°. The isolation was continued for 3 hr. The hexane extract obtained was extracted with dilute hydrochloric acid (4 *N*, 4 × 20 ml). The combined acid extracts were then washed with pure hexane (2 × 50 ml). The resulting acid solution was then covered with freshly distilled ether (50 ml), cooled, and neutralized with excess solid sodium bicarbonate. After shaking the ether layer was separated and the neutralized solution was extracted with more ether (3 × 50 ml). The combined ether extracts were dried over sodium sulfate and run through a short column (10 ml) of activated alumina (to remove alcohols). The ether extract then was concentrated carefully using low holdup distillation columns to about 8-μ volume. This whole concentrate was used in a single injection into the capillary glc column for the analysis.

Gas-Liquid Chromatography—Mass Spectral Analysis. The column used was a 500-ft long by 0.03-in. i.d. stainless steel capillary coated with Amine 220 containing 5% Igepal CO-880. The column was programmed from 70 to 100° at 1°/min and then from 100 to 170° at ½°/min. Helium was used as the carrier gas. The coupling to the mass spectrometer (a modified Consolidated 21-260 instrument) was essentially as described previously by the authors (Buttery *et al.*, 1969). The odor quality of the glc effluent was followed throughout the separation.

RESULTS AND DISCUSSION

The mass spectrum and glc retention properties of the isolated earthy aroma component from potatoes were consistent with that of an authentic sample of 2-methoxy-3-isopropylpyrazine (*cf.* Seifert *et al.*, 1970; mass spectrum, two most intense ions every 14 mass units above m/e 34 intensities in parentheses: 40 (30), 41 (25); 52 (12), 54 (10); 67 (5), 68 (12); 79 (6), 80 (7); 94 (6), 95 (11); 105 (13), 109 (5); 119 (5), 124 (21); 137 (100), 138 (10); 151 (8), 152 (38)). The capillary glc–mass spectral characterization of 2-methoxy-3-isopropylpyrazine was repeated with the basic fractions from several different batches of potatoes, including one that had been isolated 10 years previously. Sevenants (1972), in an independent study, recently reported to the authors that he has also identified 2-methoxy-3-isopropylpyrazine in potatoes by direct glc mass spectrometry.

The concentration of 2-methoxy-3-isopropylpyrazine found in potatoes was low, on the order of 1 part in 10^{10} parts of potato. This concentration is still about 50 times that of the odor threshold of this compound in water which is 2 parts in 10^{12} (Seifert *et al.*, 1970). Potatoes otherwise are very bland.

The authors were unable to confirm the presence of 2-ethyl-3-methoxypyrazine in sufficient amounts to obtain a mass spectrum. If this compound is present (there is a definite earthy odor at its retention time), we estimate that its concentration would be less than about 1 part in 10^{12}, considerably lower than the odor threshold of the ethyl compound in water solution. Sevenants (1972), in his independent study, also was unable to confirm the presence of any mass spectral detectable amount of 2-ethyl-3-methoxypyrazine.

Guadagni *et al.* (1971) carried out some careful sensory studies on the effect of adding both 2-methoxy-3-isopropylpyrazine and (separately) 2-ethyl-3-methoxypyrazine to reconstituted dehydrated potatoes. Surprisingly, the ethyl compound effectively improved the flavor of the potato products but the natural isopropyl compound did not.

2-Methoxy-3-isopropylpyrazine also has been reported to occur in peas (Murray *et al.*, 1970) and to possess a pea aroma. Measurement of the exact odor character of a compound is difficult. The odor character conveyed by a compound in a food product is also influenced considerably by the other odor components that occur in that product.

Morgan *et al.* (1972) recently reported that 2-methoxy-3-isopropylpyrazine occurs in relatively large concentrations in the cultures of the microorganism *Pseudomonas taetrolens*. Perhaps the small concentrations that occur in potatoes and peas might first be formed in the soil or on the plant or tuber surface (by this or some related microorganism) and then be absorbed into the pea or potato. The potato plant, however, is botanically related to the bell pepper plant (which produces relatively large amounts of 2-isobutyl-3-methoxypyrazine) and probably is quite capable of producing the compound itself.

During the current study a number of additional compounds were characterized (mass spectra and glc retention time consistent with authentic compound) in the volatile oil of raw potatoes that had not previously been reported. These included non-*cis*-3-enol, heptanol, octanol, octan-3-ol, and hexan-2-one.

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Correction

TYLOSIN-UREA ADDUCT RELATED TO TYLOSIN STABILITY IN CATTLE FEED

In this article by E. M. Massey and D. W. Dennen [*J. Agr. Food Chem.* **21**(1), 112 (1973)], on page 112, second column, lines 1 and 2 should read: *Anal.* Calcd for $C_{48}H_{83}N_5O_{18}$: C, 56.62; H, 8.22; N, 6.88; O, 28.28. Found: C, 56.75; H, 8.44; N, 6.61; O, 28.42. On page 113; first column, lines 2 and 3 from the bottom should read: The molecular formula, $C_{48}H_{83}N_5O_{18}$, based on that reported for tylosin (Morin *et al.*, 1970), ... Also, Table I was not published with the article and should be as follows.

Table I. Regeneration of Tylosin Activity from Livestock Feeds Containing 3% Urea

	Extract activity, μg/g feed			Tylosin activity regenerated
	Months (25°)			
Feed sample	0	1	5	5
343–376	75.0	43.1	40.8	75.2
343–380	776.0	84.0	<40.0	770.0
343–41A2	350.2	200.5	132.6	348.7
343–41B2	610.3	461.0	348.2	608.5
343–CK12	801.2	653.4	406.3	795.4