Odorous Compounds from Potato Processing Waste Effluent Irrigation Fields: Volatile Acids

Acetic, propionic, isobutyric, butyric, 3-methylbutyric, pentanoic, hexanoic, and phenylacetic acids were identified by capillary GLC–MS in the odorous free acid fraction of the volatile oil from odorous soil of potato processing effluent irrigation fields. With concentrations of up to 1000 times their odor thresholds, both butyric and isobutyric acids probably contribute most to the offensive odors of the fields. Experiments with an aqueous potato slurry showed that the same compounds were formed in anaerobic model systems in the laboratory. The formation of these compounds was reduced more than 1000-fold in model systems by using aerobic conditions.

The aqueous waste from major potato processing plants in the United States is first neutralized and treated to remove solids. The resulting effluent (up to 1000 gal/min) contains mostly dissolved matter. At one time this was run into local streams. To prevent pollution of the streams a method was developed (Smith et al., 1978) whereby the effluent was run out onto fields which are used frequently for growing crops. Although this method is generally satisfactory, the soil sometimes develops an offensive odor. The authors had previously identified the compounds skatole and geosmin as the most odorous components of the soil (Buttery et al., 1979). The next most odorous fraction, in the opinion of the authors, was that containing the free organic acids. The present work reports the identification of the components of the free acid fraction.

EXPERIMENTAL SECTION

Materials. Authentic organic acids were obtained from Eastman Organic Chemicals except for acetic acid which was obtained from Allied Chemical. Samples of odorous soil were obtained as described previously (Buttery et al., 1979). The main study was carried out on three completely different samples of odorous soil.

Isolation of Organic Acids from Soil. The soil (1 kg) was mixed with water (800 mL), acidified to pH 2 with dilute hydrochloric acid (6 N, 100 mL), and then filtered. The soil residue (in the filter funnel) was washed with freshly distilled diethyl ether (500 mL), and the ether washings were used to extract the aqueous filtrate which was then extracted further with fresh ether (200 mL). The combined ether extracts were then extracted with sodium hydroxide solution (5%, 100 mL) to isolate the acids. They were regenerated by acidification with dilute HCl (6 N) and reextracted with ether (2 × 150 mL). The ether extract was dried over sodium sulfate and concentrated (using a low hold up distillation column) to a small volume (ca. 0.2–0.5 mL) by distilling off the ether on a 50 °C water bath.

Anaerobic Laboratory Spoilage of Potato Slurry. Peeled potatoes (300 g) were blended with water (1.5 L) and the resulting potato slurry placed in a 2.8-L Fernbach flask. Water (500 mL) had been used to wash two large potatoes (by swirling the water with the potatoes in a beaker). These washings were added to the Fernbach flask to provide the microflora for spoilage. The flask containing 2 L of potato slurry was covered with aluminum foil and incubated under static conditions at 30 °C for 7 days.

Aerobic Laboratory Spoilage of Potato Slurry. This was carried out in a similar way to the anaerobic sample above with the following exceptions: (1) only half the volume (1 L) was placed in the Fernbach flask; (2) the flask was covered with a double layer of cheesecloth instead of aluminum foil to facilitate air exchange; (3) the flask was agitated on a rotary shaker at 200 rpm (2.5 cm stroke).

Table I. Free Volatile Organic Acids Found in Odorous Soil

compound[a]	concn range found in soil in ppm[b]
acetic acid	4-100
propionic acid	20-150
isobutyric acid	5-90
butyric acid	21-270
3-methylbutyric acid	6-120
pentanoic acid	20-60
hexanoic acid	1-9
phenylacetic acid	1-13

[a] Mass spectral and GLC retention data consistent with that of authentic samples run on the same instruments. [b] ppm = parts (weight) of compound per million (10^6) parts of soil.

Isolation of Organic Acids from Putrified Potato Slurry. The same extraction conditions were used for both anaerobic and aerobic samples. A portion (800 mL) of the aqueous (spoiled) potato slurry after incubation was taken, acidified to pH 2 with dilute HCl, and extracted with diethyl ether (3 × 200 mL). The ether extract was dried over sodium sulfate and the ether removed by distillation (as before) to give the concentrate (ca. 0.5 mL for the anaerobic, 0.04 mL for aerobic).

Capillary GLC–MS Analysis. A Pyrex glass capillary gas–liquid chromatography (GLC) column, 150 m long by 0.64 mm i.d., coated with Tween 20 containing 5% Igepal CO-880 was used. The column was temperature programmed from 80 to 170 °C at 2 °C/min and held at the upper limit. The carrier gas velocity was 50 cm/s. The column was coupled to a modified Consolidated 21-620 mass spectrometer through a silicone rubber membrane molecular separator.

RESULTS AND DISCUSSION

The organic acids in the fraction isolated from the odorous soil were analyzed directly using a Pyrex glass capillary GLC column combined directly with a mass spectrometer (GLC–MS). Table I lists the results found. The compounds listed had mass spectral and GLC retention data consistant with that of the authentic samples. No other components were detected except in relatively trace amounts. Three main soil samples were examined and the range of concentrations found are listed. The quantitative data are based on the measurement of GLC peak areas and although carried out with reasonable care is only meant to give a rough idea of the amounts present in a typical sample.

The major acids found were butyric, propionic, 3-methylbutyric, acetic, isobutyric, and pentanoic. All of these acids, except acetic and propionic, have vomit-sweat

Table II. Volatile Components Found in Incubated Slurry of Blended Potato Using Anaerobic Conditions

compound[a]	concn range found in slurry in ppm[b]
acetic acid	25-200
propionic acid	27-120
isobutyric acid	10-90
butyric acid	110-400
3-methylbutyric acid	22-120
pentanoic acid	0.3-12
hexanoic acid	1-4
indole	0.5
skatole	2-13
phenylacetic acid	1-14

[a] As for Table I. [b] ppm = parts (weight) of compound per million parts of aqueous potato slurry.

like odors. The odor thresholds in neutral water solution have been reported for butyric as 0.24 parts per million (ppm) (Guadagni, 1970), pentanoic acid as 3.0 ppm (Cherkinski, 1961), 3-methylbutyric acid as 5.0 ppm (Van Gemert and Nettenbreijer, 1977), and isobutyric acid as 0.05 ppm (Holluta, 1960). Because of the equilibrium between RCOOH and $RCOO^-$ and H^+, the threshold is probably very much dependent on the pH of the medium. The adsorption effects of the soil also probably play a role. The pH of the soil samples obtained was close to neutral (5.9–6.8). The odor threshold in water solution probably gives us a rough idea of the importance of each acid to the odor of the wet soil.

From the concentrations listed in Table I for butyric acid, the amount found in the soil is ca. 90–1000 times its water odor threshold. For pentanoic acid the amount found in the soil is 7–20 times its odor threshold. For 3-methylbutyric this factor is 1–24 times and for isobutyric this factor is 100–1800 times. Of the known odorous compounds butyric and isobutyric acids would thus seem to be the major contributors to the total objectionable odor after skatole (found at up to 2500 times its odor threshold; Buttery et al., 1979).

It is interesting that similar free fatty acids, as well as skatole, have been implicated in the objectionable odors from pigsties (Ohta and Ikeda, 1978). Methods developed for reducing the odors from pigsties may be useful for consideration for potato waste irrigation fields.

Model System Experiments. It was found that a slurry of blended potato (initial pH 6.1) incubated with microorganisms from potato skins, developed a similar odor to the odorous potato waste field soil when stored at 30 °C for several days under relatively anaerobic conditions. The pH of the potato slurry after incubation dropped to 5.0. Skatole and free acids were isolated and analyzed using GLC–MS to give the results listed in Table II. Geosmin was not detected, but the free acids and skatole and indole were qualitatively similar to that found in the soil. There were some relative quantitative differences, but the major acid was still butyric. The general order of the concentration of these compounds was in a range similar to that found in the soil.

It is well known that butyric acid is formed by the anaerobic bacterial degradation of starches and sugars (Henrici, 1939). In fact, this has been used as a commercial process for the manufacture of butyric acid. The other organic acids are probably formed in a similar fashion. Skatole and indole, however, as mentioned previously (Buttery et al., 1979), probably result from the degradation of tryptophan. Phenylacetic acid could result from the degradation of phenylalanine.

Possible Methods of Controlling Offensive Odor. The use of aqueous slurries of blended potato provides a simple laboratory model system with which different methods can readily be evaluated for controlling the odor development. One effective method, that was quickly found, was to use moderate aerobic conditions during the incubation of the potato slurry. After incubation (as for the anaerobic samples) such aerobic systems did not develop any objectionable odors. The pH of the aerobic slurries after incubation rose to 8.6–8.9 in contrast to those incubated anaerobically. Isolation of the free acids from the aerobic system (after acidification to pH2) showed a concentration of butyric and isobutyric acids less than 1/1000th of that found with the anaerobic system and no detectable skatole. This is fairly predictable as it is common knowledge that anaerobic conditions produce bad odors and that aerobic conditions usually do not. In the field, better aerobic conditions might be brought about by (1) prevention of the formation of ponds, e.g., by wider distribution of the effluent and by controlling the time interval between the flooding of each field; (2) increasing the porosity of the soil to minimize anaerobic conditions, and (3) following field maintenance practices that ensure high percolation of the water into the soil.

Analytical Methods. It was found, with standard solutions of skatole and free acids in water, that vacuum steam distillation continuous extraction gave a good recovery (80%) for skatole, but only a poor recovery (ca. 1%) for C_1–C_5 free organic acids. This is probably due to the high water solubility of the free acids and hence their low steam volatility. Good recovery of the free acids could be obtained by direct ether extraction with acidification to pH 2. The free acids chromatographed well on a Pyrex glass Tween 20 GLC column, and it was not necessary to convert them to their esters.

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Ron G. Buttery*
John A. Garibaldi

Western Regional Research Laboratory
Science and Education Administration
U.S. Department of Agriculture
Berkeley, California 94710

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