

Table I. Some Compounds Identified as Volatile Flavor Components of Baked Potatoes^a

Compounds	Identified by
Neutral	
1,1-Diethoxyethane (acetal)	Ir
2-Furaldehyde	Ir, ms
2-Phenylcrotonic acid	Ir
5-Methyl-2-furaldehyde	Ir, ms
Benzaldehyde	Ms
Phenylacetaldehyde	Ms
Basic	
2,5-Dimethylpyrazine	Ir, ms
2,6-Dimethylpyrazine	Ms
2-Ethyl-3-methylpyrazine	Ms
2-Ethyl-5-methylpyrazine	Ms
2-Ethyl-6-methylpyrazine	Ms
2-Ethyl-3,6-dimethylpyrazine	Ms
2-Isobutyl-3-methylpyrazine	Ms
2,3-Diethyl-5-methylpyrazine	Ms
3,5-Diethyl-2-methylpyrazine	Ms
2-Isobutyl-3,6-dimethylpyrazine	Ms

^a Identifications were based on comparison of sample spectra with spectra of authentic compounds.

baked potato aroma than does the former single compound. This conclusion was based upon the fact that these three compounds eluted as one peak from the Silicone SE-30 column. This peak, when collected, had the characteristic odor of baked potatoes. They were subsequently identified by fractionation on a Carbowax 20M

column and again on a Silicone SE-30 column attached directly to the mass spectrometer. In addition to the three compounds mentioned above, there is some mass spectral evidence that 2-ethyl-3,5,6-trimethylpyrazine was also present in the peak.

Beside the pyrazine compounds, the compound 5-methyl-2-furaldehyde, identified in our investigation, might also contribute to the total flavor of baked potatoes.

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Ametryne Metabolite in Transpired / Guttated Water from Sugarcane Shoot

An unknown ¹⁴C metabolite was found in the collected water from sugarcane grown in soil or nutrient solution treated with ametryne (ring-¹⁴C). This metabolite was not ¹⁴CO₂ or bicarbonate, but was polar, basic, and water soluble. Plants were periodically enclosed in divided air-

tight chambers separating soil/root and shoot to allow collection of ¹⁴CO₂ and the transpired/guttated water. ¹⁴CO₂ evolved from the shoot was minor relative to both ¹⁴CO₂ from soil/root and the unknown metabolite from the shoot.

Ametryne (2-ethylamino-4-isopropylamino-6-methylthio-s-triazine) is applied for selective pre- and postemergence weed control in sugarcane, pineapple, and bananas in Hawaii. Specific studies on soil or plant metabolism of ametryne in these crops are lacking. Metabolism of s-triazine herbicides has been shown to involve biological N-dealkylation (Bakke *et al.*, 1971; Kaufman and Blake, 1970; Muller and Payot, 1966; Oliver *et al.*, 1969; Shimabukuro and Swanson, 1970), chemical hydrolysis (Hamilton, 1964; Shimabukuro, 1967), amino acid conjugation (Lamoureux *et al.*, 1970), insolubilization (Shimabukuro and Swanson, 1969; Sikka and Davis, 1968), and degradation to CO₂ (Kaufman and Kearney, 1970; Knuesli *et al.*, 1969). Most studies have been conducted with the chloro-s-triazines. The only specific study on ametryne degradation in sugarcane (Hilton *et al.*, 1970) suggested absence of ametryne and hydroxyametryne (equivalent to hydroxyatrazine, 2-ethylamino-4-isopropylamino-6-hydroxy-s-triazine) in the leaf and root extracts, while more than half of the applied ametryne (ring-¹⁴C) remained unaccounted for at 13 weeks. It appears that a large proportion of the ¹⁴C disappeared, possibly in some volatile form.

In this communication we report, for the first time, the

appearance and measurement of a ¹⁴C-labeled metabolite in the transpired/guttated water derived from the shoot of sugarcane plants growing in ametryne (ring-¹⁴C) treated soil or nutrient solution.

MATERIALS AND METHODS

Sugarcane plants of variety H50-7209 were grown from seed pieces in aerated nutrient solution. When the plants (with the seed pieces removed) were 7 weeks old, each plant was transferred to 400-g Molokai soil (Typic Torrox, clayey, kaolinitic, isohyperthermic soil) in a plastic container. After transplanting, the plants were allowed to grow for 5 weeks prior to ametryne treatment. During this period, irrigation was regulated to avoid drainage from the soil. This irrigation pattern was maintained throughout the experimental period. The growth chamber was set for 12 hr of day at 30° and 12 hr of night at 19°. When the plants were 12 weeks old an aqueous solution of ametryne (ring-¹⁴C), specific activity 29.6 μCi/mg, was applied at 5 μg/g of soil in triplicate pots and was followed by irrigation. Plants grown in untreated soil were employed for background measurements. The purity of the applied ametryne (ring-¹⁴C) was assessed by liquid-liquid parti-

tioning in chloroform and by thin-layer chromatography (tlc) with three solvent systems. It was found to contain about 1% polar radioactive impurity by liquid-liquid partition and subsequent liquid scintillation analysis of the aqueous phase. This polar impurity was identified as hydroxyametryne by tlc analysis.

The potted plants were periodically enclosed in divided Plexiglas chambers to capture any volatile ^{14}C , beginning 2 days after ametryne treatment until 60 days. These chambers were designed to isolate the soil/root system from the shoot in two separate air-tight sections. CO_2 -free air at 75 ml/min was passed through the two chambers alternately (foliage chamber at night, root chamber during the subsequent 24-hr period) and bubbled through acidic (100 μl of 4 N HCl/100 ml total volume) methanol and ethanol traps held at 0° , followed by a CO_2 trap (Jeffay and Alvarez, 1961). At the end of the 36-hr measurement cycle, the transpired/guttated water which had deposited in the upper chamber was collected and measured for radioactivity. In our experimental procedure we had no means of distinguishing between transpired and guttated water from a sugarcane shoot; we have, therefore, called the collected water "transpired/guttated water." All the radioassay was done by liquid scintillation counting. The plant parts and the soil were extracted with 80% methanol (containing 100 μl of 4 N HCl/100 ml volume) at 60 days following ametryne treatment, and the extract was analyzed by thin-layer chromatography. Any ^{14}C remaining in the extracted residues of soil and plant was measured by combustion (Peterson, 1969).

RESULTS AND DISCUSSION

Nearly 21% of the total applied ^{14}C was recovered in the sugarcane plant (9.8% in the shoot), while 64% was recovered in the soil. A detailed accounting of the recovered ^{14}C was accomplished and will be presented elsewhere.

More than 1% of the total applied ^{14}C or 5.1% of the plant-absorbed ^{14}C was measured in the transpired/guttated water collected in the shoot section of the chamber during the 60-day period (Figure 1). During this same period ^{14}C activity in $^{14}\text{CO}_2$ captured from the shoot in the effluent air stream was small (0.1% of the absorbed ^{14}C) relative to that in the condensed water. Also, there was no additional activity in the ethanol or methanol traps placed in the effluent air stream. Thus the activity in the transpired/guttated water represented the major loss of ^{14}C from sugarcane shoots. No radioactivity was detected in the wash water when the lower chamber enclosing the soil/root system was rinsed, although 4% of the total applied ^{14}C was evolved as $^{14}\text{CO}_2$ from this chamber.

A separate set of experiments was conducted with sugarcane in single-compartment chambers containing whole plants (shoot and root system not separated), with the plant growing in nutrient solution to which either ^{14}C -ring-labeled ametryne or ^{14}C -ring- or ethyl chain-labeled hydroxyametryne was applied. The gaseous effluent monitoring and analyses for ^{14}C in the transpired/guttated water were the same as in the divided chamber study. The presence of ^{14}C (1.9% of the applied ^{14}C in 30 days) in the transpired/guttated water from sugarcane treated with ametryne was confirmed in these studies. On the other hand, no ^{14}C activity was found in the collected water obtained from plants treated with hydroxyametryne, suggesting that ametryne and hydroxyametryne were degraded through different pathways. This result is particularly interesting in that hydroxyametryne was one of the principal products of degradation recovered in the soil at the end of the sugarcane-soil experiment. Also, the labeled hydroxyametryne contaminant (1%) in the [^{14}C]ametryne used in these experiments evidently was not responsible for the shoot-emitted metabolite in the condensed water from ametryne-treated plants.

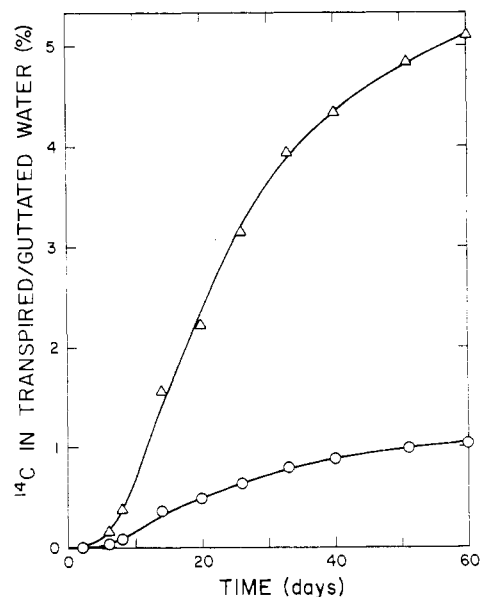


Figure 1. Cumulative ^{14}C in unknown metabolite found in the collected water from the shoot of sugarcane plant growing in soil treated with ametryne (ring- ^{14}C). Δ , % of plant uptake; \circ , % of total applied.

Preliminary attempts to identify the nature of the metabolite by tlc analysis showed that it was polar but its R_f value did not correspond with any of the commonly measured products such as ametryne, hydroxyametryne, or their partially or wholly dealkylated species including ammeline (2,4-diamino-6-hydroxy-*s*-triazine) and ammeline (2-amino-4,6-dihydroxy-*s*-triazine). No ^{14}C was lost from the collected water when it was treated with acid and bubbled with nitrogen gas for 1 hr, followed by heating in a boiling water bath for 20 min with continued bubbling of nitrogen gas. When the transpired/guttated water was made alkaline with sodium hydroxide solution while bubbling air through it for 1 hr, 57.6% of the ^{14}C was lost from the water. Heating the alkaline water in a water bath caused a further loss of 22.2% ^{14}C , leaving only 20.2% of the original radioactivity in the water. No ^{14}C was detected at any time in the CO_2 trap and in the cold ethanol and methanol traps which were employed downstream. All radioactivity measurements were corrected for quenching. These tests suggest that the unknown compound evolved from sugarcane shoot is a water-soluble base.

The measured loss of unidentified metabolite and $^{14}\text{CO}_2$ from the sugarcane shoot and the substantial loss of $^{14}\text{CO}_2$ from the soil/root system (4% of applied ^{14}C) probably explain the low recoveries reported by Hilton *et al.* (1970). The presence of a metabolite from ametryne in the transpired/guttated water from sugarcane indicates an additional, hitherto unreported mechanism by which a pesticide metabolite may be lost from plants.

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Corrections

TYLOSIN-UREA ADDUCT RELATED TO TYLOSIN STABILITY IN CATTLE FEED

In this article by Eddie H. Massey and David W. Dennen [*J. Agr. Food Chem.* 21(1), 112 (1973)], on page 112, second column, lines 1 and 2 should read: *Anal. Calcd for C₄₈H₈₃N₅O₁₈: 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 bottom should read: "The molecular formula, C₄₈H₈₃N₅O₁₈, based on that reported for tylosin (Morin *et al.*, 1970), . . ."

CARBOFURAN: ITS TOXICITY TO AND METABOLISM BY EARTHWORM (*Lumbricus terrestris*)

In this article by Jorgen Stenersen, Andrew Gilman, and Alexander Vardanis [*J. Agr. Food Chem.* 21(2), 166 (1973)], in Figure 8 on page 170, the reference compound 3-ketocarbofuran is positioned incorrectly. It should be shown between reference compounds 3-hydroxycarbofuran and carbofuran and should have an *R_f* of 0.65.

APPLICATIONS OF LASER RAMAN SPECTROSCOPY TO NATURAL PRODUCTS RESEARCH

In this article by Stanley K. Freeman [*J. Agr. Food Chem.* 21(4), 521 (1973)], Figure 14 on page 525 should have included in the caption the following reference to the source of the presented spectra: "Yu, N.-T., Liu, C. S., *J. Amer. Chem. Soc.* 94, 5127 (1972)."

CAROTENOID CONSTITUENTS OF PYRETHRUM FLOWERS

In this article by Stafford W. Head [*J. Agr. Food Chem.* 21(6), 999 (1973)], the author of the second reference in the seventh line of the second paragraph of the first column on page 999 should be Prebluda. On page 1001 of the same article the name of the first author of the tenth reference of the Literature Cited should be changed to Prebluda.