Production of Volatiles by Ripening Bananas

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The production of volatile compounds by ripening bananas was followed by gas chromatographic analysis of dynamic headspace injections. The peak areas of 17 compounds (6 acetate esters, 5 butyrate esters, 4 alcohols, 1 ketone, and 1 isovalerate ester) relative to that of an internal standard were determined. The total amount of banana volatiles followed a sigmoidal increase during ripening. In general, the amounts of individual volatiles increased continuously to the onset of peel browning, after which they either plateaued or decreased. An exception to this generality was the concentration of ethyl acetate, which increased continuously even into late senescense. A linear correlation existed between the ratio (total acetate esters)/(total butyrate esters) and ripening time. Discrepancies between these results and those of some previous workers indicate that the method chosen for volatile isolation greatly influences the results of the analysis.

Extensive work on the qualitative nature of banana volatiles involving a variety of sampling methods has resulted in the isolation and identification of some 230 compounds (van Straten and Maarse, 1983). Research also has focused on the amounts of these compounds and their patterns of production during fruit ripening. Serini (1956) studied the changes in the amounts of 2-butanol and 2,3-butylene glycol, and Hultin and Proctor (1961) extracted and identified 10 compounds at four different stages of fruit ripeness. McCarthy et al. (1963) and Wick et al. (1966) used gas chromatography to monitor 18 compounds, and several free and esterified volatile fatty acids were studied by Ueda et al. (1970).

In the early 1970s, several teams of researchers investigated the volatiles of banana fruit, using a diversity of analytical systems to continuously monitor these concentrations. Tressl et al. (1970) and Drawert et al. (1972) reported steady increases in the concentrations of individual acetate esters from ripening bananas, which eventually either plateaued or begin to decline from a maximum concentration, about 10 days after the climacteric peak. Tressl and Jennings (1972) sampled and monitored six acetate esters, five butyrate esters, and two alcohols by dynamic headspace during a period of 12 days. These authors reported that individual compounds were expelled in a cyclic fashion and that the cyclic production of total acetate esters was out-of-phase with that observed for the butyrates. By a similar sampling method, Mattei (1973) and Mattei and Paillard (1973) studied the volatiles of ripening bananas at several storage temperatures (12–30 °C). They found that the concentration of most compounds experienced a steady increase until a maximum was attained, after which strong diminution was observed.

The discrepancies in these various reports make it plausible that some of these results were affected by inadequate sampling methodologies. This paper describes the results of a work aimed at determining the relative amounts of the main volatiles of ripening bananas by a method that minimizes sample alteration and maximizes analytical efficiency.

EXPERIMENTAL SECTION

Sampling Technique. One kilogram of unripened Valery bananas (color grade 3; von Loesecke, 1950) was placed in a glass chamber (10 L) housed within a thermostated water bath (20.5 ± 0.5 °C) as shown in Figure 1. Air (99.99% pure) was introduced to the chamber at a rate of 300 mL/min, equivalent to sweeping the chamber volume approximately every 30 min. The sampling point was preceded by a mixing volume to blend the banana volatiles with vapor from methyl valerate and isopropyl propionate. After ascertaining that the ratio of peak areas for these two additives did not vary under the experimental conditions employed, the latter was used as an internal standard. A syringe with a fused silica capillary needle was used for sampling gaseous mixtures (fruit volatiles + internal standards) for a period of 50 s (100 μL/10 s). Samples were taken over a fruit storage period of 10 days.

Gas Chromatography. Samples were analyzed on a 28 m × 0.25 mm fused silica column coated with 0.25 μm of DB-1, using on-column sample injection techniques patterned after those described by Takeoka and Jennings (1984). A Varian 3700 gas chromatograph equipped with a FID (230 °C), interfaced to a Hewlett-Packard 5880 integrator for data-recording purposes, was used for the analyses. Hydrogen carrier gas was supplied at a flow rate of 1.5 mL/min; the column was held at 30 °C for the first 5 min and programmed at 3 °C/min to the end of the separation.

Table I. Banana Volatiles Shown in Figure 2

peak no.	compound[a]	peak no.	compound[a]
7	ethyl acetate	19	butyl acetate
8	isobutyl alcohol	20	2-pentyl acetate
10	butanol	25	isoamyl acetate
11	2-pentanone	33	isobutyl butyrate
12	2-pentanol	34	butyl butyrate
13	propyl acetate	41	2-pentyl butyrate
14	isopentyl alcohol	46	isoamyl butyrate
16	isobutyl acetate	49	isoamyl isovalerate
18	ethyl butyrate		

[a] Based on retention times and mass spectral data.

RESULTS AND DISCUSSION

To lend increased credence to the measurements, two internal standards were added (methyl valerate, isopropyl propionate); neither interfered with the separation of other solutes of the mixture, and their chemical functionalities are similar to those of many banana volatiles. Peak areas of other compounds were then compared to that of isopropyl propionate; on those infrequent occasions where the peak area ratio of the two standards was not constant, data were not used.

Figure 2 shows a chromatogram obtained from ripening bananas at a color grade of 7. Table I lists the 17 com-

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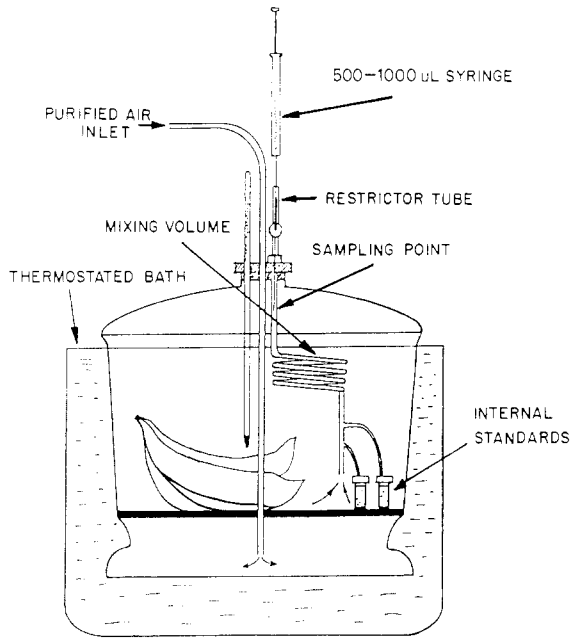

Figure 1. Equipment for dynamic headspace sampling.

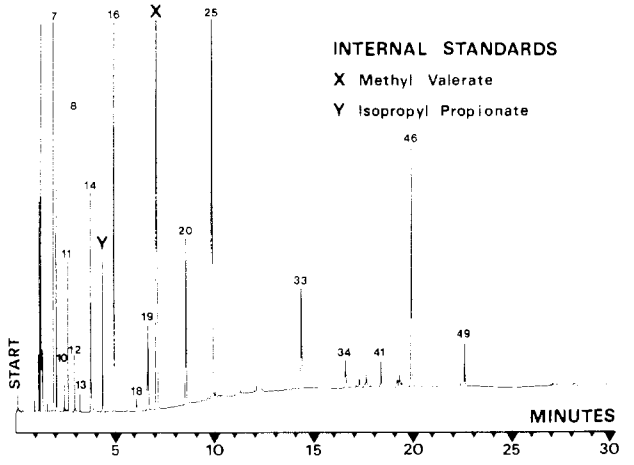

Figure 2. FID chromatogram of 500 μL of banana volatiles collected by dynamic headspace. Sample is cryogenically trapped on a 0.25 mm × 28 m DB-1 fused silica capillary column with a film thickness of 0.25 μm. Conditions: hydrogen carrier gas at 1.5 mL/min; chromatography carried out at 30 °C for the first 5 min and then at increasing temperature of 3 °C/min.

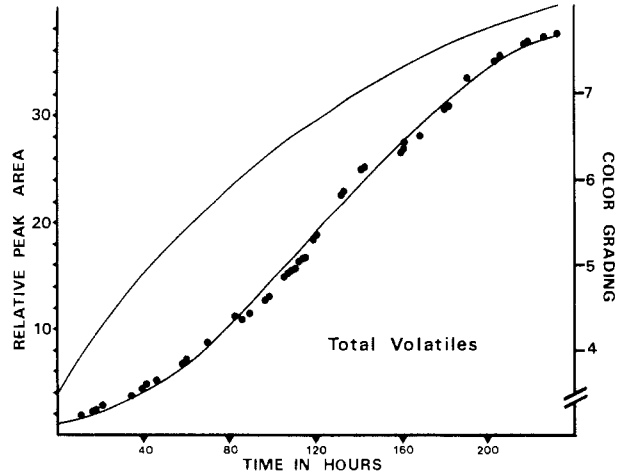

Figure 3. Total volatiles and color grading of ripening bananas. Solid line corresponds to the changes in color grading. Solid line drawn through dots corresponds to the changes in the amount of total volatiles.

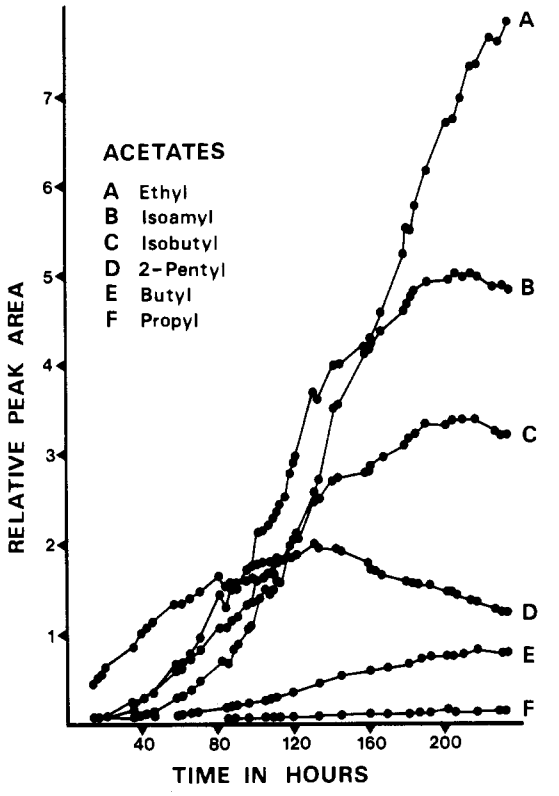

Figure 4. Levels of acetate esters from ripening bananas.

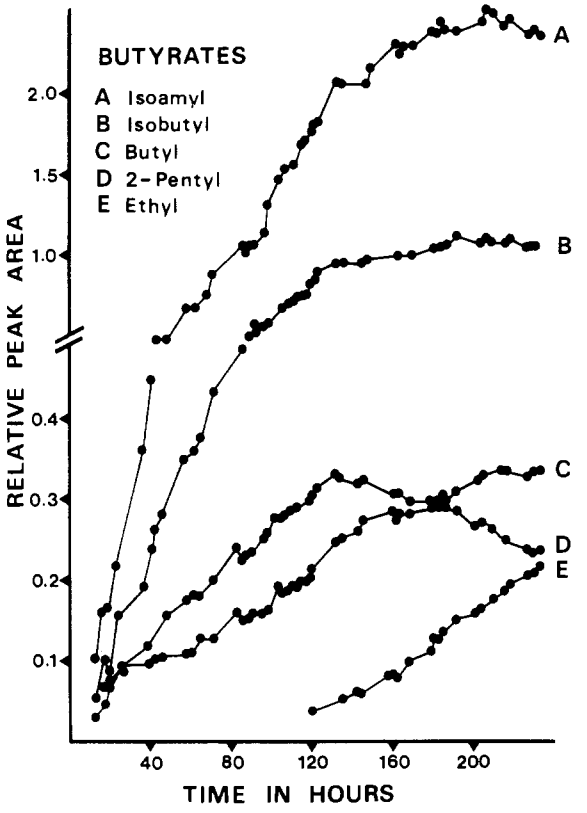

Figure 5. Levels of butyrate esters from ripening bananas.

pounds studied in this work and their order of elution from the chromatographic column.

The total amounts of volatiles, reported as relative peak areas, and the change of color grading during fruit ripening are shown in Figure 3. Total volatiles increased in a sigmoidal pattern, similar to results reported by Mattei (1973) and by Mattei and Paillard (1973) at a storage temperature of 20 °C.

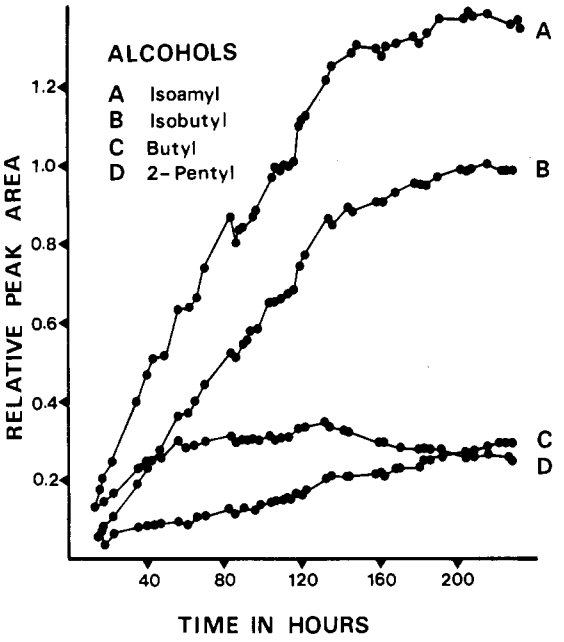

Figure 6. Levels of alcohols from ripening bananas.

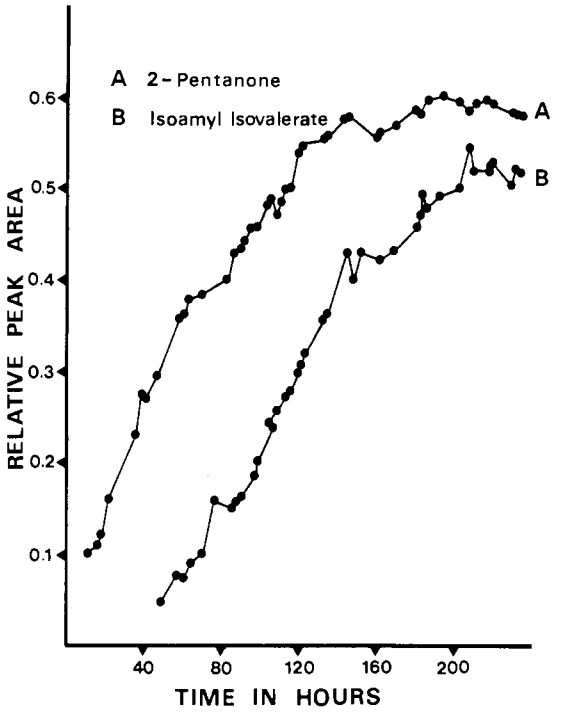

Figure 7. 2-Pentanone and isoamyl isovalerate as volatiles from ripening bananas.

The relative amounts of the main acetate esters and the main butyrate esters are shown in Figures 4 and 5, respectively. Figure 6 shows the relative amounts of the four alcohols studied in this work, and Figure 7 shows the relative amounts of 2-pentanone and isoamyl isovalerate. The relative amounts of total acetate esters and total butyrate esters are shown in Figure 8. The amounts in Figures 3–8 are intercomparable since there was a common internal standard used for all compounds. Most of the compounds increased in concentration during ripening until the bananas reach a color grade of 7 (onset of peel browning) where volatile production reaches either a maximum or a plateau. An exception to this pattern is the production of ethyl acetate, which increases into late senescence, where the fruit would normally be considered inedible. As shown in Figure 9, there was linear correlation

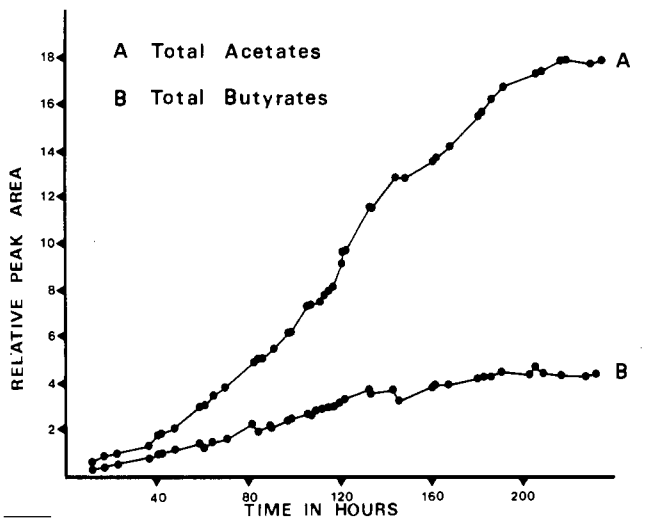

Figure 8. Levels of total acetate and total butyrate esters from ripening bananas.

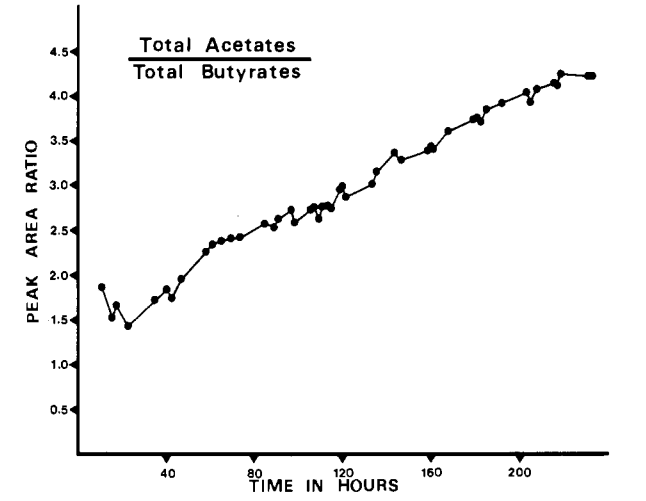

Figure 9. Ratio of total acetate esters to total butyrate esters from ripening bananas.

between the ratio (total acetate esters)/(total butyrate esters) and the time of fruit ripening (r = 0.990). This relationship between members of two groups incorporating different alkyl moieties may have biogenetic implications.

The relative amounts and production patterns of a few acetate esters were found to agree with those reported by Tressl et al. (1970) and Drawert et al. (1972). The relative amounts of 2-pentyl acetate, 2-pentyl butyrate, and ethyl acetate (especially at the postclimacteric phase) are larger than the ones reported by Tressl and Jennings (1972). These compositional differences can probably be attributed to discriminatory trapping engendered by breakthrough, incomplete recovery, and trap saturation (Wyllie et al., 1978; Jennings and Filsoof, 1977; Schreier, 1984). In general, the steady increase in concentration found for most volatiles in the present study agrees with the results reported by Mattei (1973) and Mattei and Paillard (1973) at 20 °C. However, the sudden decrease in individual volatile concentrations reported by these authors at a color grading of 7 was not found in the present study.

The total amounts of neither acetate esters nor butyrate esters followed the cyclic rates of production reported by Tressl and Jennings (1972), which they also reported for analogous compounds in Bartlett pears (Jennings and Tressl, 1974). The cyclic patterns observed by Tressl and Jennings (1972) could have been caused by errors in the sampling technique as described above or by variations in

laboratory lighting, in temperature, or in the manipulation of the headspace equipment (charge and discharge of the trapping material).

It is evident from these comparisons that the method chosen for volatile isolation plays a critical role in the relative amounts of individual volatiles isolated, which can in turn influence our concepts of the biochemical events that take place in live plant tissues. Earlier work by Tressl and Jennings (1972), based on "purge and trap" sampling methods, gave results that contradict those found in this study. Jennings and Rapp (1983) later reviewed the hazards accompanying purge and trap (e.g., breakthrough and/or incomplete recovery) and other sample workup procedures. Takeoka et al. (1986) recently established that massive rearrangements occurred in kiwi fruit volatiles stored at −10 °C. These hazards are largely avoided by direct headspace sampling, which permits a more accurate assessment of volatiles produced by living tissues than other methods we have employed.

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