# Tentative identification of volatile components of pineapple juice from varieties Red Spanish and PR 1–67[1]

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## ABSTRACT

The volatile components of pineapple varieties Red Spanish and PR 1–67 were analyzed by combination gas chromatography–mass spectrometry. Hexane extracts of juice were assayed with a 60 m × 0.32 mm cross-linked methyl silicon column. Twenty-six components, including 16 esters, 9 hydrocarbons and a furanone, were tentatively identified. Twelve of the components had never been reported in pineapple.

## RESUMEN

Identificación preliminar de los componentes volátiles del jugo de piña de las variedades Española Roja y PR 1–67.

En este trabajo se presentan los resultados obtenidos del estudio sobre los componentes volátiles del jugo de piña (ananás) de las variedades Española Roja y PR 1–67. Los extractos en hexano se analizaron usando la cromatografía de gases en combinación con espectrometría de masas en columnas de 60 m. × 0.32 mm. d.i. y de 25 m. × 0.20 mm. d.i. de silicio metilado. De un total de 45 espectros de masas examinados, se identificaron tentativamente 26 compuestos. Entre éstos se incluyen 16 ésteres, 9 hidrocarburos y una furanona. Doce de estos compuestos se informan por primera vez en la piña.


## INTRODUCTION

Pineapple [*Ananas comosus* (L.) Merr.] is the most important fruit crop in Puerto Rico. Ninety-five percent of the production, processing and marketing of fresh fruit or its canned products is managed by the Puerto Rico Land Authority. Total pineapple production in 1987-88 was 75,766 tons, with a farm value of $19.5 million (1). The Red Spanish variety accounts for approximately 85% of the total commercial plantings followed by variety PR 1–67. The latter is a hybrid from the cross Red Spanish × Smooth Cayenne. At present, canned pineapple juice constitutes the industry's primary processed product. Canned juice is produced

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exclusively from the Red Spanish and PR 1–67 varieties. Because of its excellent flavor quality, it has become the most popular juice in the local markets.

The objective of this work was to determine natural flavor components of these two varieties. This information would serve as reference material to determine the nature and cause of qualitative flavor changes in their canned juice in future studies.

Most work on the flavor composition of pineapple has been performed on the Smooth Cayenne variety, the predominant pineapple cultivar grown worldwide (8, 7). There is a lack of information on the flavor constituents of the Red Spanish and PR 1–67 varieties. Few studies have been reported on the flavor components of canned pineapple juice. Gawler (10) identified certain amino acids, sugars, volatile carbonyl compounds in canned Malayan pineapple juice. Howard and Hoffman (14) detected about 35 volatile compounds in canned Malayan pineapple.

A recent investigation in our laboratory revealed certain characteristics of juice made from Red Spanish and PR 1–67 varieties (6). Shelf life and chemical composition were studied. It was found that a single strength juice blend in 1:1 proportion from both varieties, enhanced the flavor quality of the pure Red Spanish juice, as detected by the sensory evaluation panel. It was considered desirable to gather information on the chemical constituents of the flavor of the particular canned juice.

One kilogram of pineapple juice was mixed with 500 g hexane (Fisher) 99 mol % pure. Approximately 250 ml of juice and hexane were mixed in a Sorwall Omni Mixer.[3] Speed control was set at 3 for 3 min each fraction (several fractions). The pineapple/hexane slurry was distilled under reduced pressure until all hexane was recovered. The excess water was removed in a separatory funnel. The hexane distillate was filtered through Whatman No. 4 filter paper to remove any suspended material. Anhydrous sodium sulfate was used to remove traces of water. The distillate was concentrated with a rotary evaporator (40° C under vacuum), and reduced to 1.0 ml final volume under a nitrogen gas stream.

Composition of the pineapple distillate preparation was determined with a gas chromatography/mass spectrometry (GC/MS) analytical system. Its operating conditions were as follows: a 60 m × 0.32 mm i.d., cross-linked bonded methyl silicon fused silica column (DB–Im J & W Scientific, Rancho Cordova, CA) was used at 14 psi helium head pressure. The GC program was as follows: 60° to 70° at 40°/min, 70° to 225° C at 5.0°/min; and 225° C for 0.2 min. Pineapple extract samples of 1.0

[3]Trade names in this publication are used only to provide specific information. Mention of a trade name does not constitute a warranty of equipment or materials by the Agricultural Experiment Station of the University of Puerto Rico, nor is this mention a statement of preference over other equipment or materials.

μl were injected. A Finnigan Model 4500 mass spectrometer was used: ion source temperature 180° C; Electron Impact Mode; the scans were made from 33 to 250 mass units/sec. The spectra obtained were compared to reference mass spectra libraries for the best match. Parallel samples were run on a Hewlett-Packard 5995 GC/MS system with a GC 0.2 mm i.d. × 25 m fused silica column with methyl silicon (OV-101) at He flow rate of 5 ml/min; 20° C initial temperature for 4 min.; temperature programmed at 5° C/min to a final temperature of 190° C, injection port temperature of 250° C. A hexane solvent "blank" was also run as a control against the possible presence of artifacts originating from hexane concentration during preparation of the extract.

## RESULTS AND DISCUSSION

We examined 45 mass spectra. Only 26 of these matched the published reference spectra with the highest purity and were detected with two different GC/MS systems, columns and column conditions as mentioned in Materials and Methods. The following tabulation shows compounds tentatively identified.

1. Heptane*[4]
2. Methyl benzene*
3. Methyl 2-methylbutyrate
4. Ethylbutyrate
5. Ethyl 2-methylbutyrate
6. Methyl 2-methylene butyrate*
7. Ethyl benzene*
8. Ethyl pentanoate
9. Methyl malonate
10. Methyl hexanoate
11. 1-Methyl cyclohexane*
12. Methyl 2-hexenoate*
13. Ethyl hexanoate
14. 2,4,6-trimethyloctane*
15. 5-ethyldihydro-2(3H)-furanone
16. 3,7-dimethyl-1,3,7-octatriene*
17. Methyl 2-methyl-3-oxobutyrate*
18. Methyl heptanoate
19. Methyl octanoate
20. Ethyl octanoate
21. Methyl 5-acetoxyoctanoate
22. Tetradecane*
23. Methyl decanoate
24. Ethyl decanoate
25. Hexadecane*
26. Octadecane*

Most of these compounds have been known as constituents of pineapple essence since Haagen-Smit et al. first reported on the composition of pineapple volatiles in 1945 (11, 12). With the exception of the work of Gawler (10) and of Howard and Hoffman (14), who studied the constituents of canned Malayan pineapple, all other published studies have been exclusively on variety Smooth Cayenne (2, 4, 5, 8, 15, 16, 17).

Figure 1 shows the reconstructed ion chromatogram for the Red Spanish pineapple juice essence extract on a 60m × 0.32 mm DB-1 methyl silicon fused silica column. Peaks are identified by number in the tabulation. All of the compounds listed for this variety were also detected in PR 1-67 and in a commercial canned juice produced locally.

The examination of peak 15 drew our attention to the work of several researchers who have reported furanone compounds in pineapple. Rodin

[4]Previously unreported in pineapple.

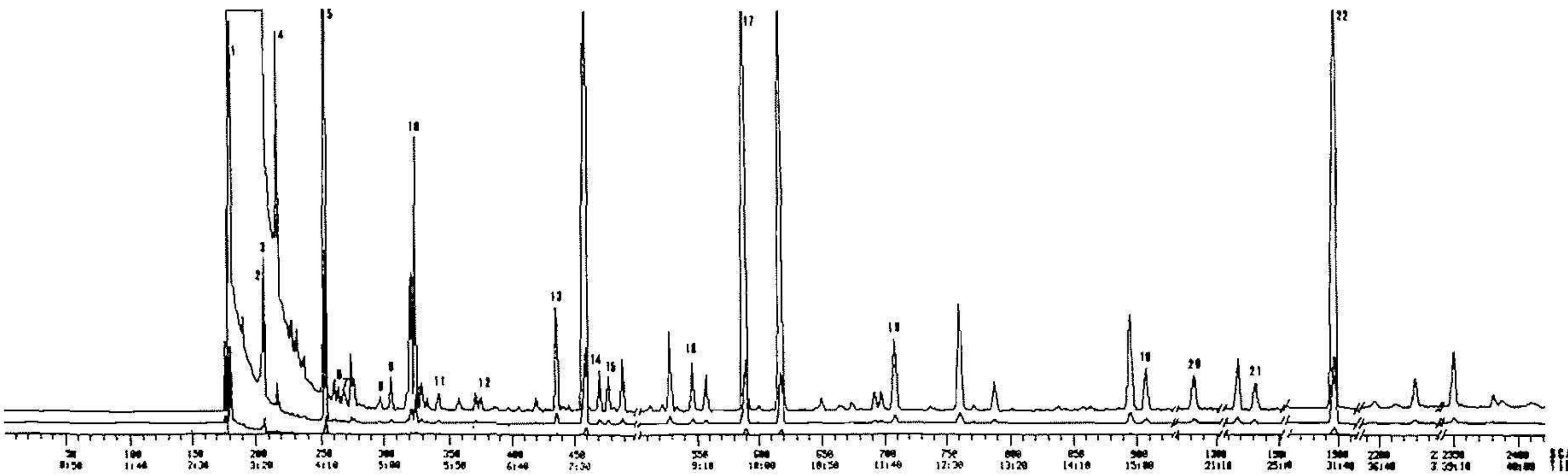

FIG. 1. Reconstructed ion chromatogram of Red Spanish pineapple juice essence extract on a 60 m × 0.32 mm DB–1 methyl silicon fused silica column.

et al. (16) isolated and identified 2, 5 –dimethyl –4– hydroxy–3(2H)–furanone which he described as having a "burnt pineapple" odor. The same compound was similarly described by Hodge et al. (13) as having a "caramel-like" odor. The presence of 2, 5– dimethyl–4–hydroxy–3(2H)–furanone was reported by Tonsbeek et al. (19) as a component contributing to beef flavor and by Buchi et al. (3) in strawberry. The mass spectra of this furanone indicated the parent peak at 128 m/e and the base peak at 43 m/e (16, 21).

In the mass spectra obtained for peak 15 of our sample the parent peak was found to be 114, thus revealing a molecular weight of 114; the base peak showed a mass of 85. The molecular weight of 5–ethyldihydro–2(3H)–furanone (α–caprolactone) is 114, and that of 2, 5 dimethyl–4–hydroxy–furanone is 128. The close similarity of the two mass spectra strongly suggests that the compound in peak 15 is identical to the α–caprolactone identified by Silverstein et al. (17) from Smooth Cayenne pineapple. This compound had not been detected previously in either Malayan or in Red Spanish varieties. This furanone has been detected in apple juice odor by Williams et al. (22); cooked asparagus aroma, Tressl et al. (20); peach aroma, Spencer et al. (18); and papaya volatile, Flath and Forrey (8) among others.

Among the outstanding components found in canned Malayan pineapple juice and in the present sample are ethylbutyrate, first reported by Gawler (10), and ethyl 2–methylbutyrate by Flath and Forrey (9). Methyl and ethyl hexanoate have been widely reported in both Malayan and Hawaiian pineapple, whereas methyl heptanoate has been reported by Flath and Forrey (8) and by Näf-Muller and Wilham (15) in the Smooth Cayenne pineapple. Another outstanding constituent found in the present pineapple extracts was tetradecane. This compound was reported by Flath and Forrey (8) in the volatiles of papaya.

It was interesting to note that two of the more outstanding fractions, peaks 17 and 22, identified as methyl 2–methyl –3– oxobutyrate and tetradecane, respectively, have not previously been reported in pineapple. Nor have the remaining 10 less prominent constituents observed in the present study. This may be due to differences in composition among varieties. Thus, the tentative identification of these components contributes not only to our understanding of the composition of the locally grown commercial varieties which are the basis of our canned juice industry, but also to the overall picture of the complicated flavor chemistry of tropical fruits and their processed products.

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