

# Volatile Components of Smooth Cayenne Pineapple

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Pineapple (Smooth Cayenne) essence was extracted with isopentane, and the resulting extract was examined by combination gas chromatography-mass spectrometry, using large-bore open-tubular columns

and a membrane-type interface. Forty-five compounds were identified, including twenty-one previously unreported in pineapple.

Pineapple [*Ananas comosus* (L.) Merr.] has been a very popular fruit throughout much of the world for many years. However, because it is a native of the tropics, fresh fruit has until recently been available only to those consumers living within roughly four to five days' surface travel time from the areas of cultivation (Collins, 1960). Even then, fruit to be transported was harvested when only one-half to three-quarters ripe. As a result, the consumer has been familiar primarily with canned fruit and fruit products, rather than with fresh ripe pineapple. However, in the past several years whole ripe fruit has become much more widely available in the continental United States, partly because of increased use of air freight, but primarily because Hawaiian growers are using improved treatment and storage conditions which permit them to ship riper fruit for longer periods of time. As a result, consumers are becoming more aware of the considerable flavor differences between fully-ripened fresh fruit and the canned product. As commonly cultivated in Hawaii, fruit is only available in quantity for approximately four or five months of the year (Collins, 1960), so fruit must be canned if pineapple is to be marketed throughout the year. Canned fruit may also be stored without difficulty, while fresh fruit is rather perishable. A composition and flavor study of pineapple was recently started in our laboratory to gather some information about those compounds which contribute to the flavor and aroma of fresh and of processed pineapple. So far this work has been conducted exclusively with the Smooth Cayenne variety, which is the most popular variety in Hawaii and most other major producing areas of the world.

The earliest composition work on pineapple volatiles was reported by Haagen-Smit and his coworkers (1945) at the California Institute of Technology. Starting with 2900 kg. of trimmed fruit, using fractional distillation and derivative preparation, they identified thirteen components. Gawler (1962), working at the Tropical Products Institute in London, used paper chromatography of derivatives to identify six volatile carbonyl compounds and acids in canned Malayan pineapple juice. Her paper does not mention the variety studied, but Singapore Spanish is the variety grown in that area for canning (Collins, 1960). In 1964, Connell reported his results with essence prepared from juice pressed from pineapple skins, cores, and trimmings at a Queensland cannery. Again, the variety was not listed, but Smooth Cayenne is widely grown for canning in that part of Australia. He employed isothermal gas chromatography with three different stationary phases, in combination with selective chemical treatment of the extracted oil for component identification. Sixteen compounds were identified. In his paper, he also

reported some earlier results obtained by Mori with an anhydrous essence prepared in Hawaii (presumably from Smooth Cayenne). Mori reportedly identified eight compounds using gas chromatographic methods, but Connell included no details of Mori's work. A series of three papers appeared in 1965 to 1966 (Rodin *et al.*, 1965; Silverstein *et al.*, 1965; Rodin *et al.*, 1966), reporting some results of a joint effort by groups at the Pineapple Research Institute (PRI) and Stanford Research Institute (SRI). This work was conducted on material obtained by ether extraction of 25 gallons of winter crop pineapple juice (Smooth Cayenne). The extract was stripped, then distilled between 25° C. to 120°, from atmospheric to 0.1 mm. pressure. A high-boiling unstable compound, 2,5-dimethyl-4-hydroxy-2,3-dihydro-3-furanone, was isolated by preparative GC and found to have a very intense odor, described as "burnt pineapple." This compound, first prepared by Hodge *et al.* (1963) from rhamnose, has since been synthesized by several groups (Willhalm *et al.*, 1965; Hofmann and Eugster, 1966), and has been reported as a flavor constituent of beef broth (Tonsbeek *et al.*, 1968). The PRI-SRI groups also identified four other pineapple components. A study using canned Malayan pineapple syrup was published by Howard and Hoffman (1967) of the Tropical Products Institute in 1967. They used head-space vapor sampling of the canned fruit syrup, with separation on three different GC liquid phases. Selective reagents were used to remove components of a given functionality from the sample, and chromatograms before and after treatment were compared. They were able to report the identity of sixteen compounds. The most recent paper on pineapple volatiles reported further results with the material extracted in the earlier PRI-SRI study (Creveling *et al.*, 1968). This work was conducted by Creveling and Jennings of the University of California, Davis, and Silverstein of SRI. The components were isolated by preparative gas chromatography, and were identified by spectral methods (IR, NMR, MS). Twelve new compounds were reported. A summary of reported pineapple volatiles is listed in Table I.

## EXPERIMENTAL

**Volatiles Concentration.** Efforts in our laboratory have so far been limited primarily to qualitative determinations, with emphasis upon identification of pineapple components. To that end, we have used pineapple essence as an initial convenient source of components. The essence was obtained from the major Hawaiian pineapple growing and processing firm, where it is produced during the preparation of frozen juice concentrate from heat-treated single strength beverage juice. The essence (9 liters) was saturated with sodium chloride, then extracted with purified isopentane (purified by stirring with several portions of fuming sulfuric acid, washing with water, then with saturated sodium bi-

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carbonate solution, and distilling through a 1-inch  $\times$  36-inch Raschig-ring column; b.p. 27.3–27.5° C.) in a large glass-Teflon liquid-liquid extractor for 24 hours. After distillation of the bulk of the solvent, the residual solution was shaken with solid sodium carbonate, filtered, and further reduced to a volume of approximately 5 ml.

**Analytical Technique.** The approach used in this study of pineapple aroma components is quite similar to that employed in previous composition investigations in our laboratory (Flath *et al.*, 1967; Flath *et al.*, 1969). Stainless steel open-tubular columns (500-foot  $\times$  0.02-inch I.D., 500-foot  $\times$  0.03-inch I.D., 1000-foot  $\times$  0.03-inch I.D.; each coated with methyl silicone oil OV-101 containing 5% Igepal CO-880) were used for all analytical separations, with the GC operating parameters chosen to provide maximum separation of extract components, as monitored with a flame-ionization detector (FID). A typical analytical run is shown in Figure 1. The columns were then transferred to a combination GC-mass spectrometer system for mass spectral examination of the column effluent. The gas chromatograph portion of the system is basically a modified Thermotrac oven (Beckman Instruments, Inc., Fullerton, Calif.), and the mass spectrometer is a QUAD 300 quadrupole instrument (Electronic Associates, Inc., Palo Alto, Calif.). The membrane-type interface enrichment device has been described by Black *et al.* (1969). It is basically a 1-square inch film of DSRE 2608 (General Electric experimental silicone polymer, 60 mole % phenyl, 40 mole % methyl substitution) painted on a fine fritted silver support, and held at approximately 165° C. This membrane has recently been replaced with a film of methyl silicone rubber (General Electric Company, Schenectady, N. Y.; 0.001-inch nominal thickness), as used by Llewellyn and Littlejohn (1966), but most of the GC-MS work reported in this paper was carried out with the DSRE 2608 membrane. The 1000-foot  $\times$  0.03-inch I.D. column was programmed from 50° to 185° C. at approximately 1° C./minute, at a head pressure of 22 p.s.i. (injector block at 170° C.). At 125° C., the helium throughput was 11 cc./minute, with an average linear velocity of 36 cm./second. Extract sample volumes of 1.5 to 2.0  $\mu$ l. were injected. With the analyzer chamber of the mass spectrometer connected directly to one side of the membrane, and with the column effluent stream passing across the opposite side of the membrane at atmospheric pressure, the MS pumping system maintained the analyzer at a helium pressure of  $1 \times 10^{-3}$  torr (gauge reading  $2 \times 10^{-6}$  torr). Continuous 0.1 second scans from *m/e* 18–206 were monitored on an oscilloscope, and the total ion current monitor (TICM) was used to provide a chromatogram for comparison with preliminary analytical FID runs. Mass spectra were recorded as they appeared on the scope, using a 1.0-second scan rate and a three-channel oscillograph. Once a component was identified from its mass spectrum, its identification was verified in two ways: First, by running a batch sample mass spectrum of authentic material on the same spectrometer and comparing spectra; and second, by co-injecting authentic sample with the volatiles mixture (FID monitoring) to compare its retention behavior with that of the tentatively-identified peak.

Some preliminary efforts were directed toward using the GC-MS system for identification of components separated during headspace analysis of fresh pineapple, but lack of overall system sensitivity limited identification to only the major lower-boiling components. Two low-boiling compounds, ethanol and methyl acetate, were identified in this manner, although they had been missed in the earlier liquid

**Table I. Reported Volatile Pineapple Components (1945–68)**

Ethyl formate <sup>i</sup>	$\Delta$ -Octalactone <sup>j</sup>
Methyl acetate <sup>a,i</sup>	Ethyl hexanoate <sup>a,d,e</sup>
$\gamma$ -Butyrolactone <sup>j</sup>	Methyl 3-hydroxyhexanoate <sup>j</sup>
1-Propyl formate <sup>i</sup>	Ethyl 3-methylthiopropionate <sup>d,h</sup>
Ethyl acetate <sup>a,d,e,i</sup>	Methyl <i>cis</i> -4(?)-octenoate <sup>j</sup>
Ethyl acrylate <sup>a</sup>	Methyl octanoate <sup>a,d,e</sup>
1-Butyl formate <sup>i</sup>	Ethyl 3-hydroxyhexanoate <sup>j</sup>
2-Methyl-1-propyl formate <sup>i</sup>	Ethyl octanoate <sup>e</sup>
1-Propyl acetate <sup>i</sup>	Pentyl hexanoate <sup>d</sup>
Ethyl propionate <sup>i</sup>	Methyl 3-acetoxyhexanoate <sup>j</sup>
Methyl butyrate <sup>e</sup>	Ethyl 3-acetoxyhexanoate <sup>j</sup>
Methyl 2-methylpropionate <sup>j</sup>	Formaldehyde <sup>e</sup>
$\gamma$ -Caprolactone <sup>a</sup>	Acetaldehyde <sup>a,c,i</sup>
Acetoxyacetone <sup>j</sup>	Acetone <sup>a,i</sup>
2-Methyl-1-propyl acetate <sup>i</sup>	2,3-Butanedione <sup>d</sup>
Ethyl butyrate <sup>d,e</sup>	2-Pentanone <sup>a</sup>
Ethyl 2-methylpropionate <sup>i</sup>	Furfural <sup>f</sup>
Methyl pentanoate <sup>a</sup>	5-Hydroxymethylfurfural <sup>f</sup>
Methyl 3-methylbutyrate <sup>a,d</sup>	2,5-Dimethyl-4-hydroxy-2,3-dihydro-3-furanone
Ethyl lactate <sup>d</sup>	Methanol <sup>d</sup>
Methyl 3-hydroxybutyrate <sup>j</sup>	Ethanol <sup>a,d,i</sup>
2-Propyl 2-methylpropionate <sup>j</sup>	1-Propanol <sup>d</sup>
Ethyl 3-methylbutyrate <sup>a</sup>	2-Methyl-1-propanol <sup>d</sup>
Methyl 4-methylpentanoate <sup>a</sup>	1-Pentanol <sup>d</sup>
Methyl hexanoate <sup>d,e,i</sup>	<i>para</i> -Allylphenol <sup>b</sup>
Dimethyl malonate <sup>j</sup>	<i>trans</i> -Tetrahydro- $\alpha,\alpha,5$ -trimethyl-5-vinylfurfuryl alcohol <sup>j</sup>
Methyl 3-methylthiopropionate <sup>b,d,h</sup>	
$\gamma$ -Octalactone <sup>j</sup>	

<sup>a</sup> Haagen-Smit *et al.*, 1945b; <sup>b</sup> Haagen-Smit *et al.*, 1945a; <sup>c</sup> Gawler, 1962; <sup>d</sup> Connell, 1964; <sup>e</sup> Mori, 1963 (see Connell, 1964); <sup>f</sup> Rodin *et al.*, 1965; <sup>g</sup> Silverstein *et al.*, 1965; <sup>h</sup> Rodin *et al.*, 1966; <sup>i</sup> Howard and Hoffman, 1967; <sup>j</sup> Creveling *et al.*, 1968.

**Table II. Pineapple Essence Extract Components**

1. Isopentane (solvent)	27. Ethyl pentanoate <sup>a</sup>
2. Ethanol	28. Methyl hexanoate
3. Methyl acetate	29. Methyl 3-hexenoate <sup>a</sup>
4. Ethyl acetate	30. Dimethyl malonate
5. 2-Methyl-3-buten-2-ol <sup>a</sup>	31. Ethyl hexanoate
6. Methyl propionate <sup>a</sup>	32. Methyl heptanoate <sup>a</sup>
7. 2-Methyl-1-propanol	33. Methyl 3-methylthiopropionate
8. 2-Propyl acetate <sup>a</sup>	34. Methyl 3-hydroxyhexanoate
9. Benzene <sup>a</sup>	35. Ethyl heptanoate <sup>a</sup>
10. Methyl 2-methylpropionate	36. Ethyl 3-methylthiopropionate
11. 3-Pentanone <sup>a</sup>	37. Linalool <sup>a</sup>
12. Ethyl propionate	38. Methyl octanoate
13. 1-Propyl acetate	39. Ethyl 3-hydroxyhexanoate
14. Methyl butyrate	40. Ethyl benzoate <sup>a</sup>
15. 1,1-Diethoxyethane <sup>a</sup>	41. Ethyl octanoate
16. 3-Methylbutan-1-ol <sup>a</sup>	42. Terpinen-4-ol <sup>a</sup>
17. 2-Methylbutan-1-ol <sup>a</sup>	43. Methyl 3-acetoxyhexanoate
18. 2-Methyl-1-propyl acetate	44. $\alpha$ -terpineol <sup>a</sup>
19. Methyl 2-methylbutyrate <sup>a</sup>	45. Ethyl 3-acetoxyhexanoate
20. Diethyl carbonate <sup>a</sup>	
21. Ethyl butyrate	
22. Methyl pentanoate	
23. Ethyl 2-methylbutyrate <sup>a</sup>	
24. Ethyl 3-methylbutyrate	
25. 3-Methyl-1-butyl acetate <sup>a</sup>	
26. 2-Methyl-1-butyl acetate <sup>a</sup>	

<sup>a</sup> Previously unreported in pineapple.

extract GC-MS run. The vapor analysis system is presently undergoing modification to improve its performance.

## RESULTS AND DISCUSSION

The 45 compounds identified so far in this study are listed in Table II. Excluding solvent, 21 of these have not been reported previously in pineapple. Conversely, 33 compounds reported by other workers have not

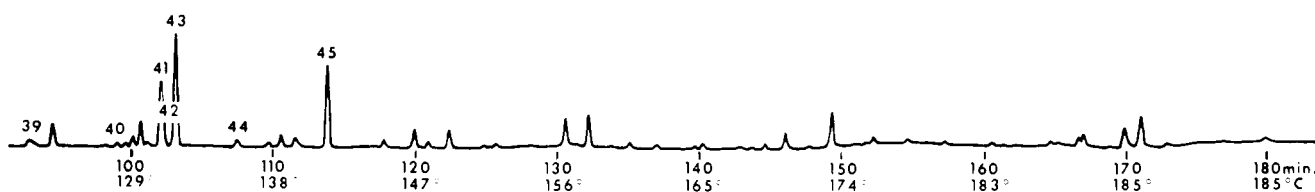
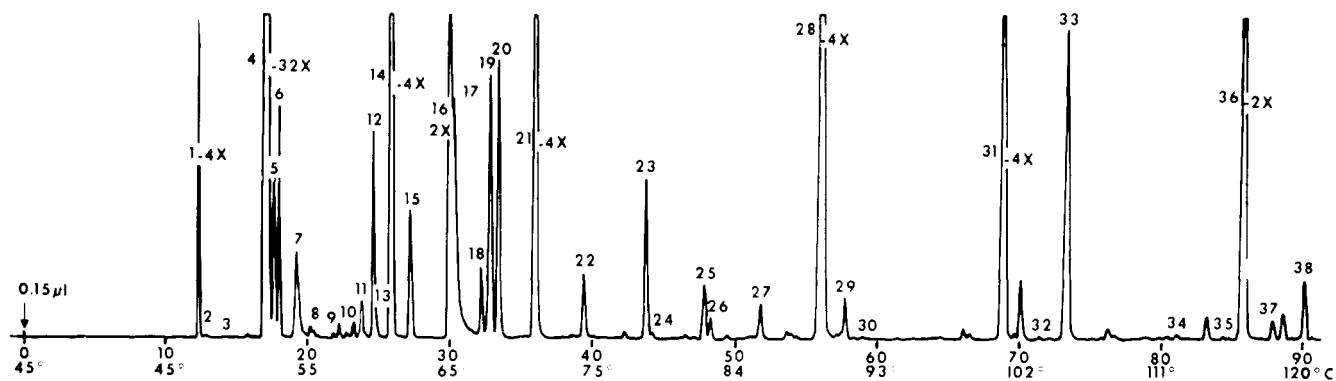


Figure 1. Analytical FID pineapple extract chromatogram

Isopentane extract of Smooth Cayenne variety. Separation on a 500-foot  $\times$  0.03 inch I.D. column, coated with methyl silicone (OV-101). Peaks are identified by number in Table I

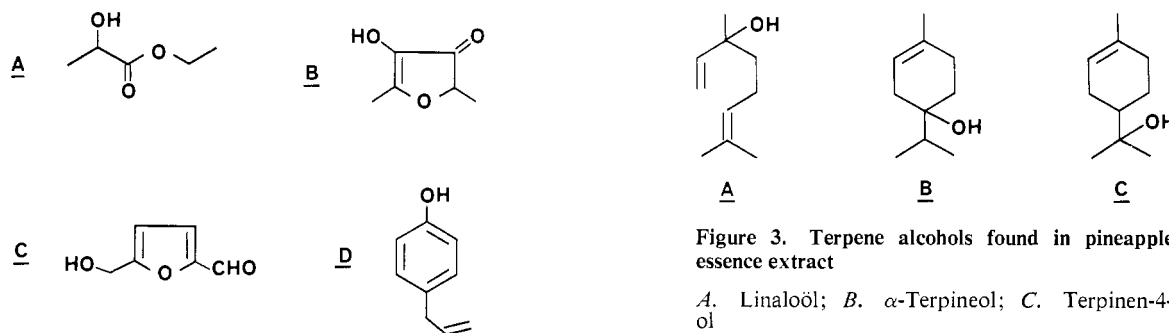


Figure 2. Reported pineapple components which did not survive injection into stainless steel open-tubular GC columns

A. Ethyl lactate; B. 2,5-Dimethyl-4-hydroxy-2,3-dihydro-3-furanone; C. 5-Hydroxymethylfurfural; D. *para*-Allylphenol

yet been detected in the essence extract, although authentic samples of most reported compounds were prepared or obtained for comparison purposes. Four of these samples (Figure 2), ethyl lactate, 2,5-dimethyl-4-hydroxy-2,3-dihydro-3-furanone, 5-hydroxymethylfurfural, and *para*-allylphenol, did not survive injection into the stainless steel open-tubular GC columns, so would not have been detected, even if present in the extract. 1,1-Diethoxyethane (acetal) did not appear in FID vapor analyses of fresh pineapple, so it is most likely an artifact in the essence. Most of the compounds identified were aliphatic esters; relatively few alcohols were encountered. This may be due in part to the choice of extracting solvent; when a portion of the essence was extracted for a longer period of time, the concentration of several lower alcohols in the resulting extract increased. The identifications of the three terpene alcohols, linalool, *alpha*-terpineol, and terpinen-4-ol (Figure 3), are considered to be fairly reliable; the mass

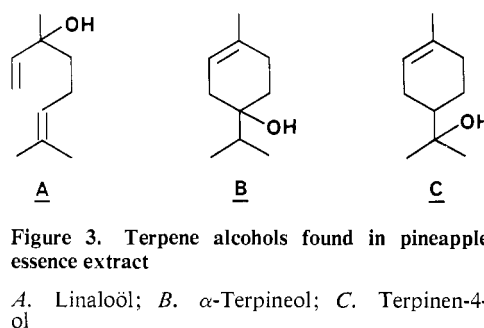


Figure 3. Terpene alcohols found in pineapple essence extract

A. Linalool; B. *alpha*-Terpineol; C. Terpinen-4-ol

spectra match those of reference samples, and the correct GC peak is increased in size on coinjection of each sample with the extract.

Numerous other components are yet to be identified, including some with molecular ions appearing in the sesquiterpene region ( $m/e = 204$ ), but most of our efforts have so far been directed toward the identification of the lower molecular weight compounds.

Gas chromatographic separation of the extract is far from complete; numerous peaks appear as poorly-resolved shoulders on other peaks. Therefore, other liquid phases of different polarity are presently being tried, with the hope that some presently-unidentified compounds will then be better separated from overlapping neighbors.

Other sources of pineapple volatiles, including fresh and canned fruit, remain to be examined. The vacuum steam distillation-extraction technique used by Buttery (1969) to considerable advantage looks promising for the concentration of higher-boiling volatiles from juice and fruit pieces. Pineapple juice rapidly forms an intractable stable emulsion when direct solvent extraction is attempted, so some alternative approach is necessary for volatiles concentration from fresh material.

#### ACKNOWLEDGMENT

The authors thank G. E. Felton and The Dole Company for generous supplies of essence and fresh fruit. Considerable helpful information was also obtained during discussions with G. E. Felton and with F. P. Boyle of WURDD.

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Received for review October 6, 1969. Accepted December 17, 1969. Presented at the 158th National Meeting, American Chemical Society, New York, N. Y., September 7-12, 1969. Reference to a company or product name does not imply approval or recommendation of the product by the U. S. Department of Agriculture to the exclusion of others that may be suitable.