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## Some Volatile Constituents of Passion Fruit

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Volatile components of the purple passion fruit (*Passiflora edulis* Sims) were extracted from the vacuum steam distillate with ethyl ether and concentrated by distillation. The concentrate was separated into an acidic and a neutral fraction, and these fractions were separated by gas chromatography. Individual components were characterized by infrared and mass spectrometry. Microhydrolysis was also used in elucidating the structures of certain of the more complex esters. Twenty

volatile compounds were identified, including 16 previously unreported in passion fruit. The majority of the compounds identified were esters, and this class included not only normal aliphatic esters but also 2-alkyl, aromatic, and unsaturated esters. Several aliphatic acids and alcohols were also identified, as was  $\beta$ -ionone. Contributions of these compounds to the passion fruit character are discussed.

The purple passion fruit (*Passiflora edulis* Sims) is a tropical fruit native to Brazil but now grown in most of the tropical and subtropical countries of the world. The unique exotic flavor is so popular that demand by processors exceeds the local supply of the fruit (Pruthi, 1963). This paper describes the isolation and characterization of the major volatile constituents of the purple passion fruit, a fruit which has not previously been investigated.

The only other study on passion fruit volatiles was done on another variety, *Passiflora edulis* flavicarpa, the yellow passion fruit (Hiu and Scheuer, 1961). In this latter study they reported that four esters, ethyl butyrate, ethyl hexanoate, hexyl butyrate, and hexyl hexanoate, comprised 95% of the volatile oil, and that hexyl hexanoate was the principal constituent. The volatiles of passion fruit wine (yellow variety) were studied by Muller *et al.* (1964) and about 20 volatile substances were found, but since this is a fermented product the results are not applicable to this study.

The juice of yellow passion fruit is orange-yellow in color, highly aromatic in flavor, and quite acid; juice of the purple passion fruit is deeper orange in color and is said to be somewhat more aromatic and less acid than the yellow (Chan *et al.*, 1972). According to Pruthi (1963) there is a real but subtle difference in flavor between the purple and yellow varieties of passion fruit, and information on the purple variety is needed.

### EXPERIMENTAL

**Sample Preparation.** Four-hundred-and-eighty gallons of a single strength New Guinea passion fruit juice (*Passiflora edulis* Sims) were vacuum steam distilled at 28.5 in. of Hg and 110°F in a commercial Centritherm evaporator to give about 15 gal of aqueous distillate possessing a distinct passion fruit aroma. This material was shipped by air from New Guinea to our laboratory.

The aqueous material was extracted in small batches with three one-third volumes of diethyl ether. The ether from the combined extracts was continuously distilled through a Vigreux column and re-used. After extraction was completed, the ether was distilled to 200 ml and this material was extracted with 5% sodium carbonate. The ethereal solution was dried and concentrated by slow distillation to give 5 ml of a yellow oil which contained the neutral components of the passion fruit juice.

The carbonate solution was acidified and extracted with ether. This ethereal extract was concentrated by distillation to yield about 2 ml of the acidic components.

**Apparatus.** Separation of the sample was accomplished using a Perkin-Elmer Model 900 gas chromatograph with a flame ionization detector. The primary separation was performed on a 6-ft  $\times$  0.125-in. stainless steel column packed with 10% diethylene glycol succinate polyester (DEGS) on 80/90 Anakrom ABS. The injector port temperature was held at 200°C and the detector was held at 225°C. The column was programmed from 80 to 200°C at 5°C per minute and held at 200°C for 6 min. The flow rate of the helium carrier gas was 30 ml per minute. Isolated components were trapped from the exit port of the chromatograph by condensation in Dry Ice-cooled capillary tubes. Purity of the isolated individual components was demonstrated by rechromatography on a nonpolar (SE-52) gc column.

The infrared spectra of the higher boiling isolated components were run as thin films between sodium chloride plates, while spectra of the lower boiling components were run as carbon tetrachloride solutions in 0.1-mm Barnes ultramicro-cavity cells. In both cases spectra were obtained using a 4 $\times$  refracting beam condenser in a Perkin-Elmer 521 spectrophotometer.

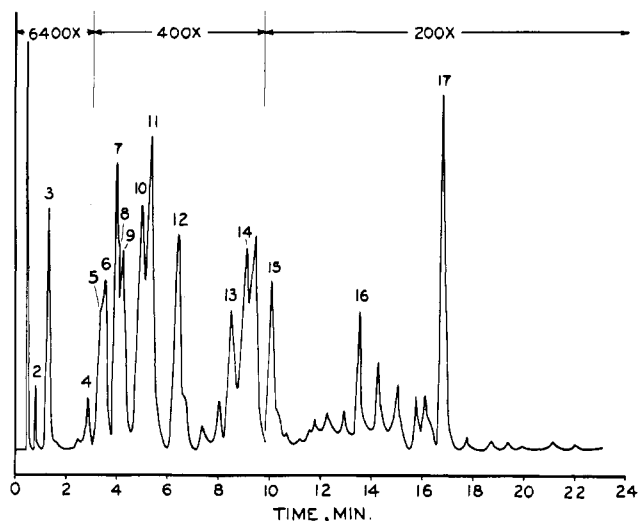
Mass spectra were run using combined gas chromatography-mass spectrometry. Column effluent passed through a fritted glass enricher (Watson and Biemann, 1965) maintained at 300°C into the ion source of a Bendix Time-of-Flight mass spectrometer. Chromatograms were recorded

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**Table I. Acidic Compounds in Passion Fruit**

Component	Relative amount <sup>a</sup>
Acetic acid	1.3
Butanoic acid	7.5
Hexanoic acid	48
A hexenoic acid, mol wt = 114	2.0
Octanoic acid	5.0
An octenoic acid, mol wt = 142	1.6

<sup>a</sup> Relative amount as determined by peak area estimated by triangulation.



**Figure 1. Gas chromatogram of neutral fraction of purple passion fruit**

from the total ion current monitor operated at 70 eV, and spectra were obtained using the 70 eV ion source also.

Evidence which was required for identification included identical gas chromatographic retention times on both a polar (DEGS) and nonpolar (SE-52) column, as well as identical mass spectra and infrared spectra between the isolated component and a known reference standard.

**Microhydrolysis.** Microhydrolysis was used in the identification of certain of the esters as suggested by Wick *et al.* (1969). The ester, which was trapped from the exit port of the gas chromatograph, was treated with 1 ml of 5% potassium hydroxide at 90°C for 45 min. This solution was extracted twice with 1-ml portions of diethyl ether; the ether was dried over sodium sulfate and concentrated carefully under nitrogen to a volume of about 0.1 ml to yield the alcohol moiety. The aqueous alkaline residue was acidified with hydrochloric acid,

**Table II. Neutral Compounds in Passion Fruit**

Peak <sup>a</sup>	Component	Relative R <sub>t</sub>	% Comp <sup>b</sup>
1	Solvent	...	...
2	Ethyl acetate	0.06	4.3
3	Ethyl butyrate	0.16	33.3
4	Ethyl hexanoate	0.46	12.3
5	Hexyl acetate	0.60	1.7
6	2-Heptanol	0.64	2.0
7	1-Hexanol	0.72	3.1
8	<i>cis</i> -3-Hexenyl acetate	0.74	1.6
9	<i>cis</i> -3-Hexenol	0.76	2.1
10	2-Heptyl butyrate <sup>c</sup>	0.90	4.0
11	Hexyl butyrate	1.00	6.0
12	<i>cis</i> -3-Hexenyl butyrate	1.18	4.0
13	2-Heptyl hexanoate <sup>c</sup>	1.62	2.6
14	Hexyl hexanoate	1.72	4.6
15	<i>cis</i> -3-Hexenyl hexanoate	1.92	1.3
16	Benzyl acetate	2.65	1.8
17	$\beta$ -Ionone	3.28	3.2

<sup>a</sup> Refers to peak in Figure 1. <sup>b</sup> Percent composition was determined using relative areas which were calculated using a PDP-8-I computer. <sup>c</sup> Microhydrolysis also indicated this structure.

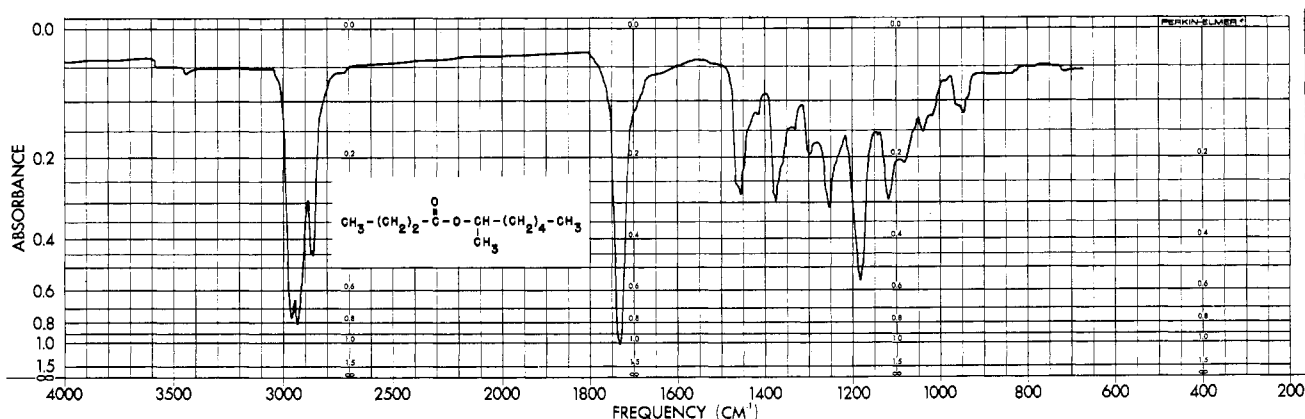
extracted, and concentrated as above to yield the acid moiety. Infrared, mass spectrometry, and gas chromatographic retention times were used to identify the hydrolysis products.

**Reference Materials.** The majority of the reference compounds required were available from commercial sources. The 2-heptyl esters were synthesized in good yield by reacting the appropriate acid chloride and 2-heptanol under anhydrous conditions in pyridine solution. High-resolution mass spectra of these two esters were recorded on a CEC-21-110 double focusing mass spectrometer using an ionizing voltage of 70 eV.

**RESULTS AND DISCUSSIONS**

The six free acids which were found to be present in the passion fruit concentrate are shown in Table I. The presence of the four saturated acids is not surprising, as these have been reported as constituents of numerous fruits (Nursten and Williams, 1967). Of interest is the high relative concentration of hexanoic acid which was found in this fraction. Two unidentified unsaturated acids were also shown to be present. Infrared and mass spectra of these compounds were both consistent with unsaturated, nonconjugated 6- and 8-carbon acids, respectively.

A chromatogram of the neutral ethereal concentrate of passion fruit is shown in Figure 1. The neutral components which have been identified are shown in Table II. The identities of these compounds were confirmed by comparison of their mass spectra, infrared spectra, and gas chromatographic retention times with those of authentic compounds recorded



**Figure 2. Infrared spectrum of 2-heptyl butyrate**

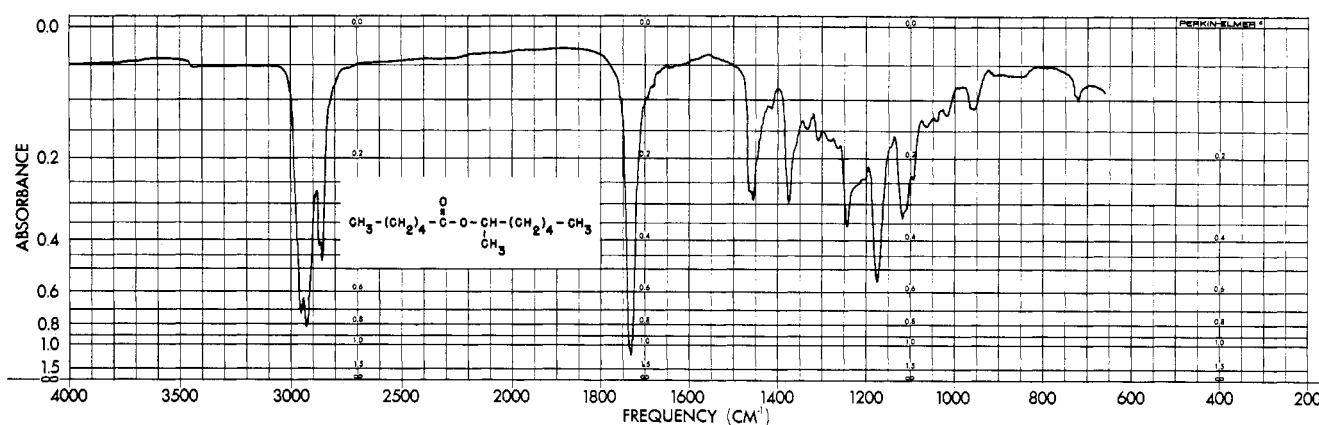


Figure 3. Infrared spectrum of 2-heptyl hexanoate

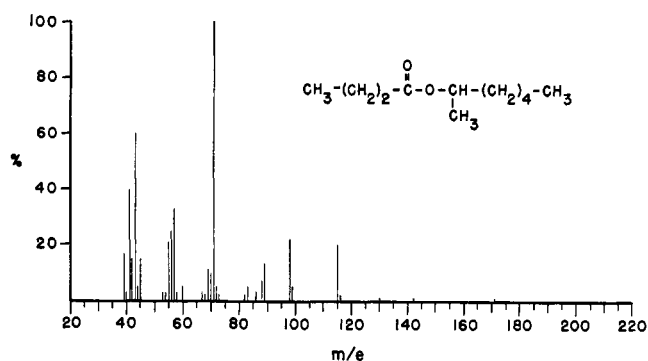


Figure 4. Mass spectrum of 2-heptyl butyrate

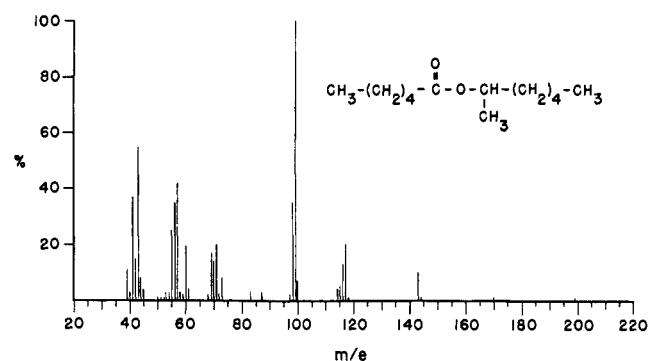


Figure 5. Mass spectrum of 2-heptyl hexanoate

under similar conditions. The approximate composition of this ethereal essence was calculated by determining relative peak areas on the chromatogram.

Since reference spectra of the 2-heptyl esters have not been previously published, infrared (Figures 2 and 3) and mass spectra (Figures 4 and 5) are included. The infrared spectra are similar to those of other higher esters; the most characteristic feature is the relatively strong band at  $1375\text{ cm}^{-1}$ . This band represents the symmetrical bending of the methyl-CH bonds and is considerably stronger in these branched esters and distinguishes them from straight chain esters. Mass spectra of both compounds give an almost imperceptible parent peak, but a discernible  $M - 15$  fragment at  $m/e$  171 for 2-heptyl butyrate and  $m/e$  199 for 2-heptyl hexanoate. In both cases, the base peak is due to cleavage next to the C=O to give  $\text{CH}_3(\text{CH}_2)_2\text{C}=\text{O}^+$  ( $m/e$  71) for 2-heptyl butyrate and  $\text{CH}_3(\text{CH}_2)_4\text{C}=\text{O}^+$  ( $m/e$  99) for 2-heptyl hexanoate.

The unique, typically tropical, mixed fruit flavor of the passion fruit is undoubtedly due to a large extent to the high concentration of esters present. In the current study, various esters were found to comprise about 80% of the total neutral essence.

Hiu and Scheuer (1961) demonstrated that ethyl butyrate represented only about 2% and hexyl hexanoate about 70% of the petroleum ether extract of the yellow passion fruit. In contrast to this, the present study shows that ethyl butyrate is the major constituent (33%) and hexyl hexanoate is a relatively minor component (5%) in the purple variety. This fact may help account for the subtle difference between the flavor of yellow and purple varieties of passion fruit. In the current study, ethyl butyrate and ethyl hexanoate comprise almost 50% of the essence, and these must contribute to the floral mixed fruit character of the juice. Unsaturated and aromatic esters together comprise about 10% of the essence,

with various *cis*-3-hexenyl esters composing 7% and benzyl acetate about 2.5%, respectively.

The relatively high concentration (>6%) of 2-heptyl butyrate and 2-heptyl hexanoate is another unusual property of this fruit. These compounds have not been reported to be common constituents of fruit aromas, although Tressl *et al.* (1970) have reported them in banana. The significant amount of  $\beta$ -ionone (3%) combined with its extremely low threshold (Buttery *et al.*, 1971) indicates that this compound must be a contributor to the overall passion fruit aroma.

Although many of the isolated constituents have intense and distinctive aromas, it is evident that no single or small number of compounds is responsible for the characteristic aroma of the purple variety of passion fruit juice. Further studies are in progress to identify the minor components which contribute to the character impact of passion fruit juice.

#### ACKNOWLEDGMENT

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