

**Method C and Proof of Structure.**—A solution of 2-acetothienone<sup>15</sup> in carbon bisulfide was brominated according to Brunswig<sup>16</sup> and afforded a good yield of  $\alpha$ -bromo-2-acetothienone. The latter compound was condensed with sodium methylmalonic ester and the reaction mixture was worked up according to the regular procedure. Attempts to purify the resulting diethyl methyl- $\alpha$ -thenoyl-methylmalonate (I) by vacuum distillation resulted in considerable decomposition. The ester (35 g.) was therefore hydrolyzed and the resulting acid (II) (10 g.) was crystallized from water. It was obtained as white crystals; m. p. 165–166° (dec.).

*Anal.*<sup>17</sup> Calcd. for  $C_{10}H_{20}O_3S$ : S, 13.22. Found: S, 13.30, 13.36.

The dicarboxylic acid was readily decarboxylated in good yield to  $\alpha$ -methyl- $\beta$ -( $\alpha'$ -thenoyl)-propionic acid, m. p. 110–111°. A mixture of this compound and the compound obtained by method B showed no depression of the melting point.

**$\alpha$ -Methyl- $\gamma$ -( $\alpha'$ -thienyl)-butyric Acid.**—Reduction of the above keto acid was carried out using amalgamated zinc and 1:1 hydrochloric acid at 25° according to the directions of Fieser and Kennelly<sup>8</sup> for the preparation of  $\gamma$ -( $\alpha$ -thienyl)-butyric acid. There was obtained an oily product (b. p. 130–135° at 15 mm.) which on cooling to 0° produced colorless crystals, m. p. 28–29°. The yield was 70%.

*Anal.*<sup>14</sup> Calcd. for  $C_9H_{12}O_2S$ : S, 17.40. Found: S, 17.53, 17.63.

**4-Keto-5-methyl-4,5,6,7-tetrahydrothionaphthene.**—The acid chloride was prepared by boiling gently for five hours a solution of  $\alpha$ -methyl- $\gamma$ -( $\alpha'$ -thienyl)-butyric acid, thionyl chloride and pyridine in absolute ether. After removal of the solvent and excess reagent, and without distillation in vacuum, the acid chloride was cyclized in carbon bisulfide by means of anhydrous stannic chloride. The reaction mixture was worked up in the usual manner and then steam distilled. Following the elimination of the solvent the cyclic ketone came over in the distillate as an oil which solidified on cooling. The material was steam

distilled a second time. It formed colorless crystals, m. p. 35–36°. The over-all yield from the acid was 35%.

*Anal.*<sup>14</sup> Calcd. for  $C_9H_{10}OS$ : S, 19.29. Found: S, 19.32, 19.36.

**4-Hydroxy-5-methyl-thionaphthene.**—The above ketone was dehydrogenated with sulfur. The reaction product was purified by distillation in vacuum, alkali extraction, and crystallization from ligroin. The substance has a phenolic odor and crystallizes from ligroin as fine colorless needles, m. p. 109–110°, yield 10–15%.

*Anal.*<sup>14</sup> Calcd. for  $C_9H_8OS$ : S, 19.52. Found: S, 19.65, 19.80.

**5-Methyl-4,7-thionaphthenequinone.**—Following the procedure of Fieser and Fieser,<sup>18</sup> the phenol was coupled with diazotized sulfanilic acid, the azo dye reduced with sodium hydrosulfite and the amine converted to the amine hydrochloride. Because of insufficient quantity the latter compound was not analyzed, but was converted directly into the quinone according to the directions of Fieser and Kennelly.<sup>9</sup> The quinone was purified by sublimation in vacuum (100° at 15 mm.). It formed yellow needles, m. p. 120–121°, over-all yield from the phenol 15%.

*Anal.*<sup>19</sup> Calcd. for  $C_9H_8O_2S$ : C, 60.65; H, 3.39. Found: C, 60.82; H, 3.63.

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#### Summary

5-Methyl-4,7-thionaphthenequinone and some related compounds have been prepared.

(18) Fieser and Fieser, *THIS JOURNAL*, **57**, 491 (1935).

(19) Microanalysis by Eleanor Werble.

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(15) Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 8.

(16) Brunswig, *Ber.*, **19**, 2890 (1886).

(17) Macroanalysis by J. C. Nichol.

[CONTRIBUTION FROM THE WILLIAM G. KERCKHOFF LABORATORIES OF THE BIOLOGICAL SCIENCES OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY]

## Chemical Studies of Pineapple (*Ananas sativus* Lindl). I. The Volatile Flavor and Odor Constituents of Pineapple<sup>1</sup>

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Our chemical knowledge of the flavors of the fleshy fruits is largely based on comparison with the smell of synthetically-obtained esters. Few investigations have been carried out with the object of isolating and identifying the substances actually present in the fruit and responsible for their flavor. The production of these substances is an expression of the metabolism going on during ripening and their accurate knowledge is of both scientific and technical value. A direct contribution is also made by substitution of the analytical chemical determination of these compounds for

the subjective scale of grading used at present in the fruit industry. In this way, the effects of climatological factors, changes in agricultural methods, and the results of breeding experiments may be investigated.

The following investigations on pineapple (*Ananas sativus* Lindl) were carried out to determine the chemical nature of the volatile constituents and, if possible, to establish a correlation between flavor and these substances. It has been observed that the taste of pineapple varies with the season in which it is grown. Although there is a great variation in individual fruits, in general the fruit grown during the summer season has a much sweeter and more fruity flavor than that of the winter crop, and it was, there-

(1) This investigation was supported by a grant from the Pineapple Research Institute of Hawaii.

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fore, decided to investigate both types of fruits separately.

The fresh fruit was subjected to vacuum distillation at 20 mm. and the volatile material condensed in a number of traps kept at different temperatures ranging from 25° to the temperature of liquid air. The small amount of oil thus obtained is typical for the pineapple flavor. From fractionation data on these oils, an immediate difference was apparent between the summer and winter fruit. The more aromatic summer fruit has a much greater volatile oil content than the winter fruit: 190 mg. per kilogram of trimmed summer fruit (1940) and 15.6 mg. per kilogram of winter fruit (1939-40). This difference is most pronounced in the low boiling fractions, mainly in the ethyl acetate and ethyl alcohol content. The acetaldehyde content, although small, was twice as great in the summer fruit, amounting to 1.35 mg. per kilogram of trimmed fruit. A similar observation was made on the fractions boiling above 100° at 745 mm. Since a slightly different method of processing was adopted in working up the 1940 winter fruit, thereby increasing the yield of the higher boiling fractions through extraction, a fresh quantity of summer fruit was distilled in 1942. The 1940 winter fruit was shown to contain 10.75 mg. of oil per kilogram of material with a boiling point above 100° at 745 mm. as compared to 17.64 mg. per kilogram for the 1942 summer fruit. These fractions were then individually analyzed for their constituents, and, if necessary, hydrolyzed with potassium hydroxide in ethylene glycol.<sup>4</sup> In all cases the identities of the original compounds or their hydrolysis products were established by the preparation of appropriate derivatives, *i. e.*, dinitrobenzoates for the alcohols, *p*-phenylphenacyl esters for the acids and 2,4-dinitrophenylhydrazones for the carbonyl compounds.

Since it was desirable to know the composition of the individual esters, chemical treatment was postponed until a thorough fractionation had segregated some of the oil components in narrow fractions.

The quantitative separation of the lower fatty acids was accomplished by utilizing the solvent partition method of Crowell.<sup>5</sup> By this method, using saturated CaCl<sub>2</sub>-KCl solution and kerosene, acetic acid remains in the aqueous solution while butyric and higher molecular weight acids go into the kerosene phase. Propionic acid, if present, would be distributed between the two phases.

In both winter and summer fruit, small amounts of sulfur-containing fractions were obtained. The negative reaction for nitrogen excludes the presence of an isocyanate.<sup>6</sup>

In order to give an over-all picture of the various components identified in the winter and sum-

mer fruit, Table I gives the approximate amounts in terms of mg. per kilogram of trimmed fruit.

TABLE I

## SUMMARY OF COMPONENTS OF THE VOLATILE OIL OF PINE-

APPLE	
Winter fruit (1939-1940)	Mg./kg. fruit
Ethyl acetate	2.91
Acetaldehyde	0.61
Methyl isocaproate	1.4
Methyl isovalerate	0.6
Methyl <i>n</i> -valerate	.49
Methyl caprylate	.75
Methyl ester of five carbon hydroxy acid	Trace
Sulfur-containing compounds	1.07
Summer fruit (1940)	
Ethyl acetate	119.6
Ethyl alcohol	60.5
Acetaldehyde	1.35
Ethyl isovalerate	0.39
Methyl <i>n</i> -propyl ketone	Trace
Ethyl acrylate	0.77
Ethyl <i>n</i> -caproate	.77
Summer fruit (1942) boiling above 100° at 745 mm.	
Acetic acid	0.49
Ethyl ester of a C <sub>5</sub> unsaturated acid	1.08
Methyl ester of a C <sub>5</sub> unsaturated acid	0.68
Methyl ester of a C <sub>5</sub> keto acid	Trace
Sulfur-containing compound	0.88

## Experimental

Fresh pineapple of the smooth Cayenne variety was supplied by the Pineapple Research Institute of Hawaii. The trimmed summer fruit (1940), amounting to 1161 kg. (total weight of whole fruit with peel and core, 1611 kg.) was cut into small pieces and was distilled from a twelve-liter Pyrex balloon flask. The distillation was carried out at 20 mm. of mercury with the still contents being kept below 40° at all times. The vapors passed through a spiral glass condenser into a flask at room temperature, through three flasks immersed in an ice-salt bath, through three receivers at -80° and finally into a trap cooled with liquid air. The condensates in the receivers held at room temperature and at the temperature of the ice-salt mixture were returned to the still and topped to remove the volatile material. By this redistillation procedure the desired volatile material was collected in the third ice-cooled receiver and the subsequent ones at lower temperature. The bulk of the desired distillation products was contained in the first receiver cooled to -80°. The liquid air trap contained only solid carbon dioxide and no liquid condensate. The oil-aqueous condensates from the traps were combined, the aqueous phase saturated with ammonium sulfate to salt out as much of the oil phase as possible and the two phases separated. The oil phase was dried over anhydrous sodium sulfate.

The trimmed winter fruit (1939-40, 995 kg. from 1450 kg. whole fruit) was treated in an analogous manner except that after redistillation of the material from the room temperature receiver, the water remaining in the still and the condensate in the ice-salt trap was extracted with ether yielding 6.4 g. of higher boiling material.

In order to obtain more working material for the smaller fractions of the volatile constituents, an additional 740 kg. of trimmed summer fruit (1942, 1089 kg. whole fruit) was distilled. In this case, the peeled fruit was run through a Waring Blendor. The juice was squeezed out in a press and the solid residue again run through the Blendor with a quantity of water. After a final pressing, the fibers which remained were discarded.

(4) Redemann and Lucas, *Ind. Eng. Chem., Anal. Ed.*, **9**, 521 (1937).

(5) Crowell, *THIS JOURNAL*, **40**, 453 (1918).

(6) Haugen-Smit, *et al.*, *THIS JOURNAL*, **67**, 1651 (1945).

TABLE II

FRACTIONATION OF 8.6 G. OF VOLATILE OIL FROM 995 KG. OF TRIMMED WINTER FRUIT (1940)

Fraction no.	Distilln. Temp., °C.	Press., mm.	Fraction wt., g.	Sapn. no.
1	40 - 58	745	0.02	...
2	58 - 64.5	745	1.40	93.2
3	64.5- 70	745	1.20	127.5
4	70 - 87	745	0.30	121.5
5	87 -109.5	745	.90	115.5
6	109.5-115	745	.60	133
7	64 - 71	100	.60	159
8	71 - 87	100	.45	158
9	87 - 99	100	1.40	163
10	99 -115	100	0.49	158
11	115 at 100.0 mm. to 123 at 52.0 mm.		0.75	175
Residue			0.00	

TABLE III

FRACTIONATION OF THE ETHER EXTRACT OF THE AQUEOUS DISTILLATE OF WINTER FRUIT (1939-1940)

Fraction no.	Distilln. temp., °C.	Press., mm.	Fraction wt., g.
12	40-60	746	0.05
13	33-41	11	.12
14	57-67	11	.07
15	67-69	11	.46
16	69-71	11	.45
17	71-79	11	.22
18	69-78	6	.31
19	78-86	6	.32
20	71-77	2	.46
21	residue		3.5

TABLE IV

CHARACTERIZATION OF ALCOHOL PART OF VOLATILE OIL AS 3,5-DINITROBENZOATE

Fraction	M. p., °C.	Mixed m. p., °C.	% Analyses		
			Carbon	Hydrogen	Nitrogen
2, 3, 4	85 - 85.5	No depr. with Et deriv.	44.80	3.28	
6	104 -104.5	No depr. with Me deriv.	42.38	2.66	12.48
9	106.5-107	No depr. with Me deriv.	42.32	2.66	12.50
10	107 -108	No depr. with Me deriv.	42.39	2.64	12.36
11	107.5-108	No depr. with Me deriv.	42.85	2.81	12.51
Ethanol	92	.....	calcd. 44.99	3.36	11.67
Methanol	108	.....	calcd. 42.49	2.67	12.39

Winter Fruit (1939-1940)

The aqueous-oil, two-phase condensate was saturated with ammonium sulfate and separated. The aqueous phase (215 g.) gave a positive test for aldehydes. A crystalline 2,4-dinitrophenylhydrazone was obtained identical with that of acetaldehyde, as shown by analyses and mixed melting point with the synthetic derivative.

*Anal.* of 2,4-dinitrophenylhydrazone<sup>7</sup>: Calcd. for C<sub>8</sub>H<sub>8</sub>N<sub>4</sub>O<sub>4</sub>: N, 24.95. Found: N, 24.75.

The total amount of acetaldehyde present in the aqueous phase is 0.585 g., as determined by triplicate quantitative determinations.

The volatile oil phase from the cold traps amounted to 8.6 g. of anhydrous oil. This oil was fractionated at atmospheric pressure through a 20-cm. Vigreux column until the lower boiling material had been removed. The remainder was then fractionated under reduced pressure. Table II gives the distillation data.

(7) Analyses in this paper were carried out by G. Oppenheimer and G. Swinehart.

The 6.4 g. of higher boiling material obtained by ether extraction gave the fractions listed in Table III.

The lowest fraction, 40-58°, contained acetaldehyde, which was absent in higher fractions, as shown by tests with fuchsin sulfite reagent.

With the exception of Fraction 2 which contained ethyl esters, the higher boiling material consisted of methyl esters (Table IV).

Fractions 9, 10 and 11 contain small amounts of a sulfur compound and analyzed for 0.11, 0.69 and 0.75% sulfur, respectively. In addition, the higher boiling fractions contained sulfur in larger amounts. Fraction 13 contained 4.67% and fractions 15 through 20 contained 16.86, 17.89, 13.36, 10.95, 2.60 and 1.10%, respectively.

The acids characterized from these fractions are listed in Table V with their derivatives. Fraction 6 was chiefly methyl isovalerate. Fraction 9 was almost pure methyl isocaproate, while fraction 10 consisted mainly of methyl *n*-valerate with a trace of a methyl ester of a hydroxyvaleric acid.

Summer Fruit (1940)

The distillation products from 1161 kg. of trimmed summer fruit (1940) consisted of an oil-aqueous mixture, which, after saturating with ammonium sulfate and separating, yielded 320.5 g. of aqueous phase and 220.3 g. of anhydrous volatile oil phase.

Acetaldehyde was identified and determined in the aqueous phase as described for the winter fruit and amounted to 1.134 g.

Most of the volatile oil phase (197.7 g. out of 220.3 g. total) was slowly fractionated at atmospheric pressure through a 24-inch Widmer column until the lowest boiling material had been removed. The residue then was distilled at atmospheric pressure through a 20-cm. air-jacketed Vigreux column, and finally the column was substituted by a 5-cm. column and stillhead and the distillation continued at reduced pressure.

A five to nine milligram sample of each fraction was hydrolyzed by heating in a glass-stoppered 3-ml. test-tube with an excess of tenth normal potassium hydroxide in

TABLE V

p-PHENYLPHENACYL DERIVATIVES OF ACID PART OF HYDROLYZED FRACTIONS

Fraction	M. p., °C.	Mixed m. p., °C.	% Analyses	
			Carbon	Hydrogen
2, 3, 4	108 -109	108 -109	75.56	5.73
Acetic acid	108 -109		calcd. 75.57	5.56
6	71.5- 72	71 - 72	77.60	6.78
Isovaleric acid	74.0- 74.3		calcd. 77.00	6.80
9	69.5- 70	69.5- 70	77.34	7.12
Isocaproic acid	70 - 70.5		calcd. 77.20	7.45
10 (1st deriv.)	67.5- 68	68 - 69	77.45	6.98
10 (2nd deriv.)	98 - 99		73.96	6.43
<i>n</i> -Valeric acid	69		calcd. 76.97	6.82
Hydroxyvaleric acid			calcd. 73.03	6.47
11	63 - 64	63 - 65	78.16	6.86
<i>n</i> -Caprylic acid	67		calcd. 78.07	7.75

ethylene glycol. After hydrolysis, the excess base was back titrated with one-hundredth normal hydrochloric acid. From the data, saponification numbers were cal-

culated, expressed as the apparent molecular weight if the entire fraction were an ester. Table VI contains the distillation data and the saponification numbers of the fractions obtained.

TABLE VI

FRACTIONATING OF 197.7 G. OF VOLATILE OIL CORRESPONDING TO 1042 KG. OF SUMMER FRUIT (1940)

Fraction no.	Distilln. temp., °C.	Press., mm.	Fraction wt., g.	Sapn. no.
S-1	up to 69	745	4.3	162
S-2	69 - 70.0	745	116.8	118
S-3	70.0- 70.4	745	41.7	123
S-4	70.4- 75.5	745	7.3	175
S-5	75.5- 76	745	6.6	439
S-6	76 - 77.5	745	1.9	958
S-7	77.5- 78.0	745	0.4	1213
S-8	78.0- 78.7	745	.9	790
S-9	78.7- 78.8	745	.8	1289
S-10	78.8- 79.0	745	.8	889
S-11	79.0- 81.0	745	.4	1790
S-12	81.0- 88.0	745	trace	698
S-13	88.0- 89.8	745	0.4	1232
S-14	89.8- 91.0	745	.4	1001
S-15	91.0- 94.0	745	.5	311
S-16	36 - 98.5	100	.3	289
S-17	98.5-101.5	100	.8	234
S-18	101.5-105	100	.8	263
S-19	105 -109	100	.5	245
S-20	109 at 100 mm. to 124.5 at 61 mm.		.5	302
S-21	124.5 at 61 mm. to 125 at 20 mm.		.4	323

**Identification of Fraction S-1.**—This fraction was found to contain 9% of acetaldehyde, thus accounting for 0.388 g. In addition, there was 0.044 g. of acetaldehyde in the unfractionated oil, making a total of 1.566 g. in the summer fruit. Fraction S-1 also contained ethyl acetate, which was identified as before. From the saponification value, the quantity of ethyl acetate can be calculated to be approximately 55% of the fraction, which with the 9% aldehyde leaves 36% to be accounted for by the ethyl alcohol which was found to be present.

*Anal.* of 2,4-dinitrophenylhydrazone: Calcd. for  $C_8H_8N_4O_4$ : N, 24.95. Found: N, 24.72.

*Anal.* of 3,5-dinitrobenzoate: Calcd. for  $C_8H_8N_2O_6$ : C, 44.99; H, 3.36. Found: C, 44.76; H, 3.22.

*Anal.* of *p*-phenylphenacyl ester: Calcd. for  $C_{10}H_{10}O_2$ : C, 75.57; H, 5.56. Found: C, 75.71; H, 5.61.

**Identification of Fractions S-2, S-3 and S-4.**—These fractions consist of a mixture of mainly ethyl alcohol and ethyl acetate. From the saponification values the ethyl acetate content can be calculated to be approximately 75, 71.5 and 50%, respectively.

**Identification of Fraction S-5.**—This fraction gave upon hydrolysis ethyl alcohol and an acid portion yielding a low melting mixture of *p*-phenylphenacyl esters. Accordingly, the acid portion was therefore separated by partitioning between a saturated  $CaCl_2$ -KCl solution and kerosene.<sup>5</sup>

By identifying the acids after the separation, it was found that the esters originally present were ethyl acetate and ethyl isovalerate. The following quantitative results were obtained in this separation: 2.000 g. of fraction 5 was saponified with excess potassium hydroxide, the mixture acidified to pH 3 with sulfuric acid and distilled until all the organic acid had distilled over. This distillate was carefully neutralized with standard base and the solution dried to constant weight. It was found that 0.00274 equivalent of base was used and 0.3068 g. of potassium salts was obtained. From this, it can be calculated that

the 2.000 g. of fraction 5 consists of: 0.118 g. or 5.9% ethyl isovalerate, 0.162 g. or 8.1% ethyl acetate and 1.720 g. or 86% ethyl alcohol (by difference).

The dried potassium salts of the mixed acids were moistened with water, and to the solution was added an amount of standard hydrochloric acid equivalent to the amount of organic acids present. The solution was then partitioned between kerosene and saturated  $CaCl_2$ -KCl. The phases were carefully separated, and the kerosene treated with silver sulfate to remove halogen ions and then distilled. The kerosene-organic acid distillate was titrated with standard base, and it was found to require 0.000776 equivalent. This amount multiplied by the factor 1.12 (determined by Crowell,<sup>5</sup> to be a correction factor for losses in the partitioning procedure) yields 0.000869 equivalent or 0.113 g. calculated as ethyl isovalerate. This checks well with the previous figure of 0.118 g. calculated from the potassium salt mixture. The neutral aqueous phase obtained by titrating the kerosene-organic acid distillate, was made acid with a drop of sulfuric acid and refluxed with ethyl alcohol and *p*-phenylphenacyl bromide. A derivative was formed which was identified as the isovaleric acid compound.

*Anal.* of *p*-phenylphenacyl ester of isovaleric acid, m. p. 73.5-74.5°: Calcd. for  $C_{13}H_{20}O_2$ : C, 77.00; H, 6.80. Found: C, 76.84; H, 6.62.

The saturated  $CaCl_2$ -KCl solution was diluted with ethyl alcohol and, after filtering off the salts, the *p*-phenylphenacyl ester was formed as before. Acetic acid was identified in this material.

Fractions S-6 through S-11 proved to be practically all ethyl alcohol. In addition, they contained traces of esters which were not identified because of the small amounts.

**Identification of Methyl *n*-Propyl Ketone.**—Since fraction S-13 gave a positive ketone test, it was shaken with an aqueous hydrochloric acid solution of 2,4-dinitrophenylhydrazine. A small amount of crystalline material was obtained which was extracted with ether. After removal of the ether, this material was recrystallized from aqueous ethanol and yielded orange-yellow needles that melted over a range of 126-134°. This was dissolved in purified carbon tetrachloride and passed through a 50-cm. column of magnesium oxide.<sup>6</sup> Two bands developed: a fairly narrow upper band and a diffuse lower band. The colored bands were eluted with ethyl alcohol. Only very small amounts of the purified products were obtained. The derivative from the upper band melted 70-100°, while that from the lower band melted at 141-142°. The latter gave no depression with the 2,4-dinitrophenylhydrazine of methyl *n*-propyl ketone (m. p. 139.5-140.5°).

Thus, while not enough material was obtained for micro-analysis, the data accumulated indicate the presence of methyl *n*-propyl ketone. Fractions 12, 14 and 15 contain the substance in such small amounts that no appreciable amounts of derivative could be obtained from this.

Fractions S-16, S-17 and S-18 contained esters of ethyl alcohol as determined by the formation of the characteristic 3,5-dinitrobenzoates.

The acid part of fraction S-17 gave a *p*-phenylphenacyl derivative, melting at 109-110°, which turned orange when melted. This analyzed as the derivative of acrylic acid.

*Anal.* of *p*-phenylphenacyl ester: Calcd. for  $C_{17}H_{14}O_2$ : C, 76.69; H, 5.26. Found: C, 76.13; H, 5.58.

The acid part of fraction S-18 gave a *p*-phenylphenacyl derivative melting at 69.5-70°. A mixed melting point with the derivative (m. p. 70.8-71°) of *n*-caproic acid gave 67.5-69.5°.

*Anal.* of *p*-phenylphenacyl ester: Calcd. for  $C_{20}H_{22}O_2$ : C, 77.39; H, 7.14. Found: C, 76.96; H, 7.26.

Fractions S-16 through S-21 contained sulfur, ranging from 0.09% in fraction S-16 to a maximum of 3.30% in fraction S-20. Fraction S-21 contained 2.17% of sulfur.

(6) Strain, THIS JOURNAL, 57, 758 (1938).

## Summer Fruit (1942)

Since the ether extract of the water distillate from the winter fruit yielded a considerable quantity of high boiling material, this technique was applied to a fresh quantity of summer fruit (1942). Fractionating of the total volatile oil from this fruit yielded the data in Table VII.

TABLE VII  
FRACTIONATING OF 215.3 G. OF VOLATILE OIL FROM 740 KG. OF TRIMMED SUMMER FRUIT (1942)

Fraction no.	Distilla. temp., °C.	Press., mm.	Fraction, wt., g.
F-1	35-45	745	14.4 (mainly residual ether)
F-2	45-55	745	5.1
F-3	68-76	745	181.3
F-4	48-55	123	3.44
F-5	45-50	11	1.37
F-6	50-60	11	1.31
F-7	60-70	11	1.25
F-8	70-80	2	0.82
F-9	80-83	at 2	
		at 1	.50
F-10	Residue	..	5.2

Since fractions F-4 and F-5 were decidedly acidic, they were washed with dilute potassium hydroxide solution. The neutral residues were combined and fractionated as shown in Table VIII. Likewise, the acidic fractions were combined and fractionated, as shown in Table IX.

TABLE VIII  
FRACTIONATION OF NEUTRAL PORTION OF FRACTIONS F-4 AND F-5 OF THE SUMMER FRUIT (1942)

Fraction no.	Distilla. temp., °C.	Press., mm.	Fraction, wt., g.
N-1	76 - 81.5	745	0.097
N-2	81.5 - 87.5	745	.089
N-3	87.5 - 90	745	.085
N-4	90 - 95	745	.067
N-5	95 - 100	745	.161
N-6	76 - 82	100	.108
N-7	90 - 100	100	.128

TABLE IX  
FRACTIONATION OF ACIDIC MATERIAL FROM FRACTIONS F-4 AND F-5 OF THE SUMMER FRUIT (1942)

Fraction no.	Distilla. temp., °C.	Press., mm.	Fraction wt., g.
A-1	87-98	745	0.026
A-2	53-55	120	3.261
A-3	54-64	100	0.366
A-4	65-44	100	
		to 10	0.115

**Identification of Fractions A-2 and A-3.**—The presence of mainly acetic acid in both fractions was shown by preparing the *p*-phenylphenacyl derivatives.

*Anal.* of *p*-phenylphenacyl ester, m. p. 109.5-110; Calcd. for  $C_{10}H_{14}O_2$ : C, 75.57; H, 5.56. Found: C, 76.12; H, 5.38.

**Identification of Fraction F-8.**—The alcohol part of this ester fraction was identified as ethyl alcohol (3,5-dinitro-

benzoate, m. p. 90.8-91, no depression with synthetic ethyl derivative).

The *p*-phenylphenacyl ester of the acid part melted at 122-123.2° and turned yellow after melting. Analysis indicated that it was an acid with five carbon atoms and one double bond. Eleven structures for the acid are possible. The *p*-phenylphenacyl esters of two of the possible acids, tiglic and angelic, did not melt at the same temperature as the naturally occurring acid, and did not turn yellow after melting.

**Identification of Fraction F-9.**—The alcohol part of the esters did not contain ethyl alcohol, but was identified as methyl alcohol by conversion to the 3,5-dinitrobenzoate, m. p. 98.5-102°. A mixed melting point with synthetic ethyl 3,5-dinitrobenzoate gave a melting point of 70-90°, and with synthetic methyl 3,5-dinitrobenzoate (m. p. 108°) a melting point of 104-107°.

The acid part was chiefly the same  $C_6$  unsaturated acid as occurred in the fraction immediately previous, fraction F-8. It also contained a small amount of an acid, whose *p*-phenylphenacyl derivative melted at 109.5-110.5°. This analyzed as the derivative of a  $C_8$  keto acid.

*Anal.* of *p*-phenylphenacyl derivative, m. p. 109.5-110.5°; Calcd. for  $C_{10}H_{14}O_4$ : C, 74.07; H, 6.17. Found: C, 74.92; H, 6.15.

## Summary

The chemical composition of the volatile oil from fresh pineapple has been investigated, and a comparison made between the oils from the winter and summer crops.

The volatile oil content of summer fruit (1940) is 190 mg.; that of winter fruit (1939-40) is 15.6 mg. per kg. of trimmed fruit. This larger yield for the summer fruit is chiefly caused by the larger percentage of low boiling material, consisting of ethyl acetate and ethyl alcohol, respectively, 119.6 mg. and 60.5 mg. per kg. of trimmed fruit. The difference in amounts of the higher boiling material was not so pronounced. The winter fruit contains 10.75 mg. of oil boiling above 100° at 745 mm. per kg. of trimmed fruit, compared to 17.64 mg. for the summer fruit.

In addition to ethyl alcohol and ethyl acetate, the following compounds were found in the summer fruit: acetaldehyde, ethyl isovalerate, methyl *n*-propyl ketone, ethyl *n*-caproate, ethyl acrylate (probably), acetic acid, an ethyl ester of a  $C_6$  unsaturated acid, some methyl ester of the same acid, and an ethyl ester of a  $C_5$  keto acid.

The winter fruit contained, besides ethyl acetate, the following: acetaldehyde, methyl isocaproate, methyl isovalerate, methyl *n*-valerate, a methyl ester of a  $C_5$  hydroxy acid and methyl caprylate.

Both the winter and summer fruit contained a sulfur-containing compound which was present in the higher boiling fractions.

Except for the ethyl acetate, all the remaining esters investigated in the winter oil were methyl esters. In the summer fruit, only one methyl ester was found.