2. Sulfur in the *ortho* position has a decided auxochrome effect, the shift being toward the blue. As the molecular weight of the alkyl group increases, much of this effect is lost. Oxidation of sulfide to sulfone destroys whatever auxochrome effect the sulfur had.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE NON-VOLATILE ACIDS OF THE PEACH

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According to Kunz and Adam,[1] the peach contains citric acid but no malic or tartaric acid. Bigelow and Dunbar[2] state that their analyses showed that the peach probably contains only malic acid and that the question of the acids of peaches must be left open, the widespread assumption that this fruit contains malic acid as the predominating acid being shaken by the researches of Kunz and Adam.

As the nature of the acids in peaches remained in doubt, an investigation was conducted in the Bureau of Chemistry to determine just what acids are present.[3]

Water-packed sliced peaches (18 kg.) were boiled with water and pressed and the juice was concentrated. The pectin precipitated by alcohol was removed by filtration and the filtrate was treated with lead acetate in slight excess. The precipitate of lead salts was collected on a filter, washed with water and decomposed with sulfuric acid, the excess of sulfuric acid being removed with barium hydroxide.

The filtrate from barium sulfate was concentrated, water was removed by repeated evaporation with alcohol, and the residue of acids was esterified by refluxing for five hours with absolute alcohol containing 2.5% of hydrogen chloride.

After removing the alcohol by distillation, the operation was repeated with a fresh quantity of alcoholic hydrogen chloride, the alcohol was again removed, and the esters were purified by solution in ether and washing with a solution of sodium hydroxide.

The ether was evaporated and the esters were submitted to distillation at 10mm. pressure when the following fractions were collected.

Fraction	1	2	3	4
Temp., °C.	97–120	120–140	140–160	160–165
Yield, g.	1.91	4.80	3.63	8.30

[1] Kunz and Adam, *Z. Nahr. Genussm.*, **12**, 670 (1906).

[2] Bigelow and Dunbar, *J. Ind. Eng. Chem.*, **9**, 762 (1917).

[3] The volatile acids of the peach have been fully investigated by Power and Chesnut, THIS JOURNAL, **43**, 1725 (1921).

Re-fractionation at the same pressure

Fraction	1	2	3	4	5
Temp., °C.	87–90	90–120	120–130	130–155	155–165
Yield, g.	0.91	1.31	5.48	1.10	8.15

The specific rotation of Fraction 3 was —9.66°, which is close to the specific rotation for pure ethyl *levo* malate, given in Beilstein as —10.18° to —10.64°.

The acids were identified in these fractions by means of the hydrazides.[4] To 0.7 g. of the ester, dissolved in 3.5 cc. of absolute alcohol, 0.5 cc. of hydrazine hydrate was added.

Fraction 1.—The hydrazide melted at 174–178° and gave no depression with *l*-malic dihydrazide. A small quantity of more soluble hydrazide, which was not further examined, was formed.

Fraction 2.—The hydrazide melted at 175–178° and was therefore *l*-malic dihydrazide.

Fraction 3.—The hydrazide melted at 177–179° and showed no depression when mixed with *l*-malic dihydrazide.

Fraction 4.—Impure *l*-malic dihydrazide was given.

Fraction 5.—The hydrazide melted, not sharply, at 145° and showed no depression when mixed with citric trihydrazide.

The trihydrazide of citric acid also melted, although not sharply, at 145°, which is much higher than the melting point of 107° for citric trihydrazide found by Curtius.[5] In their work on the acids of the apple, Franzen and Helwert[6] separated citric trihydrazides melting as high as 125°. They believed that these higher melting points were due to contamination with malic dihydrazide. It would be strange that such contamination should *raise* the melting point. The fact that their higher-boiling fractions, which should contain less ethyl malate, give the hydrazides of higher melting point does not seem to agree with this assumption.

Summary

The non-volatile acids of the peach consist principally of a mixture of *l*-malic acid and citric acid in almost equal proportions.

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[4] *J. prakt. Chem.*, **51,** 180, 353 (1895).

[5] Curtius, *J. prakt. Chem.*, **95,** 246 (1917).

[6] Franzen and Helwert, *Z. physiol. Chem.*, **127,** 19 (1923).