Summary

The behavior of β,β'-dichloro-diethyl ether, under definite conditions, with aromatic primary amines, the sodium salts of phenol, thiophenol and naphthols, potassium phthalimide and dry sodium hydroxide has been studied and several of the resulting compounds have been described.

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

THE NON-VOLATILE ACIDS OF THE STRAWBERRY, THE PINEAPPLE, THE RASPBERRY AND THE CONCORD GRAPE

BY E. K. NELSON

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Kunz and Adam[1] state that strawberries and raspberries contain citric acid but no malic acid. Krzizan and Plahl[2] and Krzizan[3] found only citric acid in raspberries. Kayser[4] reports citric acid as the principal acid of raspberries, but found malic and tartaric acids also. Jorgensen[5] found that citric acid predominates in raspberries, with a little malic acid and traces of succinic acid but no tartaric acid. Muttelet[6] states that strawberries and raspberries contain citric acid, with traces of tartaric acid but no malic acid. Paris[7] reports the presence of citric acid and a little malic acid in strawberries. Kayser[8] states that the pineapple contains citric acid but no malic or tartaric acid. Bigelow and Dunbar[9] found in the red raspberry probably citric acid alone (malic acid, if present, in traces only). C. Garino-Canina[10] calls attention to the presence of malic acid in the grape and concludes that the relative proportion depends on geographical area and meteorological conditions.

In view of the conflicting nature of these statements in the literature regarding the non-volatile acids of fruits, an investigation was undertaken to determine, by the ester-distillation method, the character of the nonvolatile acids in strawberries, pineapples, raspberries and grapes.

[1] (a) Kunz and Adam, *Z. Osterr. Apoth. Ver.*, **44**, 187 (1906). (b) *Z. Nahr. Genussm.* **12**, 670 (1906).

[2] Krzizan and Plahl, *ibid.*, **11**, 205 (1906).

[3] Krzizan, *Z. Offentl. Chem.*, **12**, 323, 342 (1906).

[4] Kayser, *ibid.*, **12**, 155, 191 (1906).

[5] Jorgensen, *Z. Nahr. Genussm.*, **13**, 241 (1907).

[6] Muttelet, *Ann. fals.*, **2**, 383 (1909).

[7] Paris, *Chem.-Ztg.*, **26**, 248 (1902).

[8] Kayser, *Z. Offentl. Chem.*, **15**, 187 (1909).

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

[10] Garino-Canina, *Ann. chim. applicata*, **5**, 65 (1916).

Experimental Part

The technique of the investigations was identical with that used in the investigation of the non-volatile acids of the peach.[11]

Strawberry.—The esters from the acids of 19.3 kilograms of fresh strawberries, fractionated at 10 mm., yielded the following results.

Fraction	1	2	3	4
Boiling point, °C.	115–125	125–135	135–167	167–169
Weight, g.	0.5	6.0	2.8	74.4
M. p. of hydrazide, °C.	173–177	178–179	170–173	148–150

The hydrazide from Fractions 1 and 2 is *l*-malic dihydrazide, giving no depression when mixed with *l*-malic dihydrazide. The hydrazide from Fraction 3 is a mixture, and that from Fraction 4 is citric trihydrazide, giving no depression in melting point on mixing with a sample of the pure substance. These results show that the acids of the strawberry consist of a mixture of about 10% of malic acid with about 90% of citric acid.

Pineapple.—The esters obtained from 9 kilograms of pineapples canned in their own juice afforded the following results on fractionation at 10 mm.

Fraction	1	2	3	4
Boiling point, °C.	110–120	120–130	130–160	160–170
Weight, g.	0.6	2.6	0.3	22.2
M. p. of hydrazide, °C.	172–175	177–179	166–172	145 (Not sharp)

The hydrazides of Fractions 1 and 2 gave no depression in melting point when mixed with *l*-malic dihydrazide, Fraction 3 is a mixture and Fraction 4 gave a hydrazide showing no depression in melting point when mixed with citric trihydrazide. The acids of the pineapple, therefore, consist of a mixture of *l*-malic acid (about 13%) with citric acid (about 87%).

Red Raspberry.—Fractionation at 10 mm. of the esters derived from the acids of 18 kilograms of red raspberries gave the following results.

Fraction	1	2	3	4	5
Boiling point, °C.	110–115	115–130	130–145	145–160	160–170
Weight, g.	0.5	0.5	0.7	2.2	89.0
M. p. of hydrazide, °C.	175–178	175–178	170–174	162–167	140–145

By the mixed-melting-point method, Fractions 1 and 2 were shown to be ethyl malate, Fractions 3 and 4, mixtures of ethyl malate and ethyl citrate, and Fraction 5, practically pure ethyl citrate. Evidently, then, the acids of the red raspberry consist principally of citric acid (about 97% and *l*-malic acid (about 3%).

Black Raspberry.—An investigation of the acids from the black raspberry failed to show the presence of any *l*-malic acid; 99% of the es-

[11] THIS JOURNAL, 46, 2337 (1924).

ters boiled at 168–170° (10 mm.). The hydrazide melted at 148–150° The acid of the black raspberry is therefore citric acid.

Concord Grape.—The esters of the acids from 19 kilograms of Concord grapes afforded the following results on fractionation at 10 mm.

Fraction	1	2	3	4	5	6	7
Boiling point, °C....	80–90	125–130	130–140	140–145	145–150	150–155	Residue
Weight, g.....	0.6	27.0	3.0	1.5	7.7	9.0	2.7
α_D.....	.....	−9.42	−6.37	−2.4	+7.0	+7.5	...
M. p. of hydrazide, °C.....	174–176	175–178	167–170	162–167	180–182	180–184	...

The hydrazides from Fractions 1 and 2 were shown, by mixed melting points, to be *l*-malic dihydrazide, those from Fraction 3 to be impure *l*-malic dihydrazide, those from Fraction 4 to be a mixture, and those from Fractions 5 and 6 to be *d*-tartaric dihydrazide.

The relative proportions of the two acids, calculated from the optical rotations of the fractions, were about 60% of *l*-malic acid and about 40% of *d*-tartaric acid.

Summary

By the ester-distillation method it was found that the acids of the strawberry were citric acid (about 90%) and *l*-malic acid (about 10%) and that the pineapple acids were citric acid (about 87%) and *l*-malic acid (about 13%); that in the red raspberry the acids were a mixture of citric acid (about 97%) with *l*-malic acid (about 3%); and in the black raspberry the acid was citric acid. The acids of the Concord grape were a mixture of *l*-malic acid (about 60%) and *d*-tartaric acid (about 40%).

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

THE EQUILIBRIUM BETWEEN CREATINE AND CREATININE, IN AQUEOUS SOLUTION. THE EFFECT OF HYDROGEN ION

BY GRAHAM EDGAR AND H. E. SHIVER

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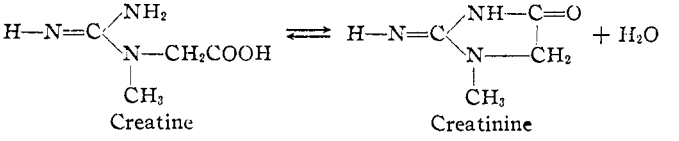
I. In Aqueous Solution

Introduction.—The reversible reaction



Creatine Creatinine (1)

is of interest not only from its importance in biochemistry, but also because of the ease with which it is adapted to physicochemical study. The