salt with the calculated amount of cinchonine sulfate, filtering the solution and concentrating the filtrate in a vacuum distilling flask.

The salt crystallized slowly from the concentrated solution, and most of the impurities could be removed by washing with a little cold alcohol. While this salt is easily soluble in warm water or alcohol, it crystallizes with some difficulty. The crystals are not immediately soluble in *cold* water or alcohol; hence, it was purified by washing with a little cold alcohol.

The cinchonine salt crystallizes in fine, pointed needles and melts with decomposition at 159–160°; Ehrlich reports 158°. The alcoholic filtrate from the barium salt was evaporated. It gave a small amount of a brown, amorphous substance from which no galactose could be isolated.

The pectic acid described by Wichmann and Chernoff is, therefore, digalacturonic acid (A), the characteristic nucleus of pectic substances.

Conclusion

The pectic acid obtained by Wichmann and Chernoff's method for determining pectin in fruit products is identical with the digalacturonic acid (A) of Ehrlich and Sommerfeld.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

DICARBOXY-PHENYLARSONIC ACIDS
I. 2,3-DICARBOXY-PHENYLARSONIC ACID AND ITS ANHYDRIDE

BY CLIFF S. HAMILTON AND RALPH FRAZIER

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Very little study has been made of phthalic acids containing an arsonic acid group on the nucleus. Only isophthalarsonic acid or 2,4-dicarboxyphenylarsonic acid has been prepared and no derivatives have been studied. Michaelis prepared the acid by oxidizing 2,4-dimethylphenylarsonic acid with potassium permanganate in alkaline solution,[1] but no reference can be found in the literature to dicarboxy-phenylarsonic acids that have been obtained by the introduction of the arsonic group into a phthalic acid nucleus.

It was of interest, therefore, to prepare 2,3-dicarboxy-phenylarsonic acid from *o*-phthalic acid. This was accomplished by first nitrating *o*-phthalic acid, then reducing the nitro compound to 3-amino-*o*-phthalic acid, and finally introducing the arsenic by means of Bart's method.[2]

The properties of 2,3-dicarboxy-phenylarsonic acid are very similar to those of monocarboxy-phenylarsonic acids. It has no melting point up to 270°, decomposition starting at approximately 220°. It is very slightly soluble in either hot or cold alcohol, insoluble in ether, but highly soluble in either hot or cold water. The free acid may be recrystallized as colorless

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[1] Michaelis, *Ann.*, **320**, 335 (1902).

[2] Bart, Ger. pat., 250,264 (1910); *Ann.*, **429**, 55 (1922).

needles from water or glacial acetic acid, but best by dissolving in hot water and adding an excess of hydrochloric acid.

The anhydride of 2,3-dicarboxy-phenylarsonic acid was formed when the free acid was heated at high temperatures. When the anhydride was condensed with resorcinol it formed a fluorescent compound resembling fluorescein. Condensation with phenol resulted in the formation of a solution resembling phenolphthalein, colorless in acid solution and pink in alkaline solution.

Further study of dicarboxy-phenylarsonic acids and their derivatives is now being carried out in this Laboratory.

Experimental Part

3-Nitro-*o*-phthalic Acid.—This was prepared by heating 185 g. of phthalic anhydride with a mixture of 175 cc. of nitric acid (d., 1.42) and sulfuric acid (d., 1.84), on a steam-bath for three hours.[3] The mixture was poured into water which dissolved the more soluble 4-isomer and left 3-*o*-phthalic acid as light yellow crystals. These were filtered off and washed with 300 cc. of water. The crude 3-*o*-phthalic acid was then distilled with benzene until the distillate was clear, to remove the excess of water and nitric acid; m. p., 198°; yield, 80–85%.

3-Amino-*o*-phthalic Acid.—This was made by the reduction of the corresponding nitro compound with tin and hydrochloric acid, while the temperature was kept at 20° and the mixture stirred in order to prevent local heating. Decomposition resulted when the temperature was allowed to rise above 30°.[4] The amino compound crystallized from the reducing mixture as the hydrochloride. It was dissolved in water and recrystallized by the addition of an equal volume of concd. hydrochloric acid. The portion remaining in solution was recovered by saturating the solution with dry hydrogen chloride. The product thus obtained was used in the preparation of the arsonic acid, after being dried under reduced pressure over sodium hydroxide to remove the excess of hydrochloric acid; yield, 45–50%. Because of conflicting data on this compound it was analyzed.

Anal. Subs., 0.5162, 0.4937: AgCl, 0.3527, 0.3433. Subs., 0.5314, 0.5018: 32.6, 31.65 cc. of 0.0714 *N* HCl. Calcd. for $C_8H_8O_4NCl$: N, 6.43; Cl, 16.30. Found: N, 6.14, 6.31; Cl, 16.47, 16.54.

2,3-Dicarboxy-phenylarsonic Acid.—Twenty-five g. of the hydrochloride of 3-amino-*o*-phthalic acid was dissolved in 500 cc. of water containing 23 cc. of hydrochloric acid (d., 1.18) and diazotized with 9 g. of sodium nitrite in 100 cc. of water, the temperature being kept below 0°.

The diazo solution was slowly added, during constant stirring, to a solution containing 75 g. of sodium arsenite, 5 g. of copper sulfate, and 25 g. of sodium hydroxide in 600 cc. of water, the temperature being allowed to rise to 20°. After the diazo solution had all been added, the mixture was stirred for one hour. It was then boiled until nitrogen was no longer evolved, made acid to Congo red paper, and evaporated to dryness. The residue was dried at 150° for several hours to remove the excess of acid, pulverized, and the soluble inorganic salts were extracted with 100 cc. of water at 0°. The residue was then treated with 100 cc. of water and 20 cc. of ammonium hydroxide and the mixture filtered. When the filtrate was made acid to Congo red paper and an excess of 20 cc. of hydrochloric acid was added, the *o*-phthalarsonic acid separated as light

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[3] Littmann, THIS JOURNAL, **47**, 1980 (1925).

[4] Bogert and Jouard, *ibid.*, **31**, 484 (1909).

brown crystals. The acid was purified by dissolving in boiling water, decolorizing with charcoal and recrystallizing by adding one-fourth the volume of hydrochloric acid. The free acid separated as colorless crystals which decomposed without melting when heated; yield, 50–55%. A sample, recrystallized from water, was dried at 98°.

Anal. Subs., 0.2043, 0.2043: 29.0, 29.3 cc. of 0.0490 *N* I soln. Calcd. for $C_8H_7O_7As$: As, 25.86. Found: 25.61, 25.85.

The NEUTRAL TRISODIUM SALT was prepared by dissolving 2,3-dicarboxy-phenylarsonic acid in the calculated amount of 0.5 *N* sodium hydroxide solution and filtering into absolute alcohol. The salt separated as an oil and was crystallized under reduced pressure.

Anal. Subs. (dried at 120° for five hours), 0.1990, 0.2047: 23.3, 23.9 cc. of 0.0483 *N* I soln. Calcd. for $C_8H_4O_7AsNa_3$: As, 21.07. Found: 21.14, 21.13.

The ANHYDRIDE of 2,3-dicarboxy-phenylarsonic acid was prepared by heating the free acid for one week at 200°.

Anal. Subs., 0.2050, 0.2090: 31.1, 32 cc. of 0.0483 *N* I soln. Calcd. for $C_8H_5O_6As$: As, 27.57. Found: 27.53, 27.78.

Summary

2,3-Dicarboxy-phenylarsonic acid has been made and studied, and its neutral sodium salt and anhydride have been prepared. A further study of the dicarboxy-phenylarsonic acids and their derivatives is now being carried out in this Laboratory.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE REACTIVITY OF HALOGENATED ETHERS

I. HALOGENATED DIETHYL ETHERS AND ZINC

BY F. NEHER AND C. L. FLEECE

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The halogenated ethers resemble the alkyl halides in their reactivity to such reagents as metals, alcoholic and aqueous potassium hydroxide, lime and sodium ethylate. But the reactions of the alkyl halides, as shown by Nef,[1] vary remarkably with temperature, concentration and the nature of the solvent, poor yields and a mixture of products being obtained. The reagent may remove two atoms of the halogen or the halogen acid; unsaturated products may be formed or addition products. An investigation of the behavior of zinc with alcoholic solutions of the halogenated ethers discussed in this paper and others to follow has shown that these compounds are much better suited to a study of the mechanism of the reactions of organic compounds of the halogens since the metal may have an entirely selective action and remove halogen or halogen acid, exclusively. A general mechanism for this selective action has been found by an examination of tetra-, tri-, di- and monochlorodiethyl ethers and some new bromo and bromochloro ethers.

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[1] Nef, *Ann.*, **298**, 330 (1897).