

2. The compound melts at 30°. Its specific rotation,  $[\alpha]_D$ , is about 420°.

3. The rotatory dispersion of the compound is large, ranging from +260° through +785° to -590°. The dispersion agrees closely with the values calculated from Drude's equation.

4. A diazo compound has also been prepared, in small amounts and in a less pure condition, from the "di-urea" *trans*-aminocamphonic acid. Its properties agree, roughly, with those of the diazo compound from the *cis* acid but the evidence on this point is incomplete.

5. It has been pointed out that an electronic interpretation of the Angeli-Thiele formula for the aliphatic diazo compounds shows a close analogy between these compounds and the aromatic diazonium compounds.

6. The diazo compound passes almost quantitatively into the bis-hydrazone of camphonic acid on standing for a short time. This reaction is closely analogous to the coupling reactions of aromatic diazonium compounds.

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

## PECTIC ACIDS

By E. K. NELSON

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F. Ehrlich and R. V. Sommerfeld, in their exhaustive investigation on the constitution of the pectic substances of the sugar beet,<sup>1</sup> apply the term "pectin" to the material, usually called "protopectin," which is not soluble in cold water, but is dissolved by hot water.

According to Ehrlich and Sommerfeld, this "pectin" is hydrolyzed by hot water into "hydropectin," which can be separated by 70% alcohol into soluble araban and the calcium-magnesium salt of pectic acid which is not dissolved. On treating this salt with hydrochloric acid in the cold and precipitating with alcohol they obtain the free pectic acid  $C_{43}H_{62}O_{37} + 10H_2O$  which, after hydrolysis for several hours with 2% hydrochloric acid on the water-bath, yields methyl alcohol, acetic acid, arabinose, galactose, an insoluble digalacturonic acid (A) and a soluble digalacturonic acid (B). They conclude that beet pectic acid is a triacetyl-arabino-galacto-dimethoxy-tetragalacturonic acid. The digalacturonic acids are formed from two molecules of galacturonic acid by the elimination of water between the aldehyde groups and hydroxyl groups of the adjacent molecule. The insoluble modification (A) has the formula  $C_{10}H_{14}O_8(COOH)_2H_2O$ .

Wichmann and Chernoff in their method for determining pectic acid

<sup>1</sup> Ehrlich and Sommerfeld, *Biochem. Z.*, **168**, 263-323 (1926).

in fruit products,<sup>2</sup> which is used as a check on the pectin determination, employ a treatment similar to that used by Ehrlich in his preparation of digalacturonic acid (A) except that they use an alkaline hydrolysis with dil. sodium hydroxide solution, followed by boiling for five minutes with dil. hydrochloric acid. The present investigation was conducted for the purpose of establishing the identity of Wichmann and Chernoff's pectic acid with digalacturonic acid (A).

One hundred g. of citrus pectin was dissolved in water and hydrolyzed with dil. sodium hydroxide solution for 15 minutes at room temperature, then acidified with hydrochloric acid in suitable excess and boiled for five minutes according to Wichmann and Chernoff's procedure. The insoluble precipitate was filtered and redissolved in dil. sodium hydroxide solution and the operation was repeated. The acid was filtered off, washed with water until the filtrate gave a negative reaction for chloride, and finally with alcohol and ether. The resulting material was dried in a vacuum desiccator; yield, 39 g.

One g. requires 52.9 cc. of 0.1 *N* sodium hydroxide solution for neutralization. Ehrlich states that his digalacturonic acid (A) required 54.0 cc.; calcd. for  $C_{10}H_{14}O_8 \cdot (COOH)_2 + H_2O$ : 54 cc.

One g. of the acid was neutralized with sodium hydroxide solution and diluted to 100 cc. This solution was used for the determination of specific rotation;  $[\alpha]_D^{20} = +289.5^\circ$ . Ehrlich reports  $+272^\circ$  to  $+285^\circ$ .

Mr. C. F. Gersdorff of this Bureau kindly made an analysis of the acid, with the following results.

*Anal.* Subs. (dried at  $110^\circ$ ), 0.3339:  $H_2O$ , 0.1500;  $CO_2$ , 0.4818. Calcd. for  $C_{12}H_{16}O_{12} + H_2O$ : H, 4.86; C, 38.92. Found: H, 4.99; C, 39.35.

On hydrolysis of digalacturonic acid with dilute sulfuric or oxalic acid at 2 to 3 atmospheres ( $130\text{--}140^\circ$ ), Ehrlich<sup>3</sup> obtained galacturonic acid which responded to the tests given by glucuronic acid (reduction of Fehling's solution in the cold, and the orcinol, resorcinol, phloroglucinol and naphthoresorcinol reactions) and yielded a characteristic cinchonine salt crystallizing in fine, pointed needles and melting, with decomposition, at  $158^\circ$ . Under the conditions described above, Wichmann and Chernoff's pectic acid yielded an acid which is easily soluble in alcohol and water but is unstable, easily oxidizing or polymerizing to a black, tarry or humin-like material. It gives the naphthoresorcinol reaction and reduces Fehling's solution in the cold. Efforts to produce a crystalline cinchonine salt by saturating its solution with cinchonine were unsuccessful. This salt was prepared through the barium salt as follows.

The acid solution, after autoclaving, was neutralized with barium hydroxide solution and filtered from barium sulfate or oxalate. The filtrate was concentrated somewhat in a vacuum-distillation outfit and then treated with an excess of alcohol which precipitated the barium salt as a yellow, water-soluble powder.

*Anal.* Calcd. for  $Ba(C_6H_9O_7)_2$ : Ba, 26.23. Found: 25.92.

The cinchonine salt was prepared by treating an aqueous solution of the barium

<sup>2</sup> Wichmann and Chernoff, *J. Assoc. Official Agr. Chem.*, **8**, 129 (1924).

<sup>3</sup> Ehrlich, *Chem. Z.*, **41**, 198 (1917).

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-dicarboxy-phenylarsonic 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,<sup>1</sup> 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.<sup>2</sup>

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

<sup>1</sup> Michaelis, *Ann.*, **320**, 335 (1902).

<sup>2</sup> Bart, *Ger. pat.*, 250,264 (1910); *Ann.*, **429**, 55 (1922).