Summary

1. 7-Methyl-4-isopropyl-3-hydroxythionaphthene was prepared from sodium cymene sulfonate.

2. Four new thioindigoid dyes containing an isopropyl group were prepared.

3. The production of a thioindigo dye from crude sodium cymene sulfonate on a semi-technical scale was made.

4. Fastness tests and spectrum analyses of the dyes were made.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH, UNIVERSITY OF PITTSBURGH]

THE ISOLATION AND IDENTIFICATION OF *d*-MANNURONIC ACID LACTONE FROM THE MACROCYSTIS PYRIFERA

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That alginic acid is a polymer of one or more aldehyde sugar acids was demonstrated by the authors in a previous communication.[1] It was shown at the same time that it is composed, at least in part, of *d*-mannuronic acid. The identity of this uronic acid was established on the basis of the fact that on oxidation it formed a dibasic acid whose diamide and diphenylhydrazide corresponded in properties to the analogous compounds prepared from pure *d*-mannosaccharic dilactone.

At the time of our earlier paper we had not succeeded in obtaining the aldehyde acid in crystalline condition and were consequently unable to publish any data on the physical properties of the new compound. The present paper describes experiments which led to the preparation of crystalline *d*-mannuronic lactone and the determination of its melting point and optical rotation.

The extraction of alginic acid from the fronds of the *Macrocystis*, as well as the method of hydrolysis and subsequent preparation of the barium and cinchonine salts of the hydrolysis product, has been previously described.[1] The yield of pure cinchonine salt was much less than the calculated amount based on the weight of the barium salt from which it was prepared. The mannosaccharic acid formed, in poor yield, after oxidation of the barium salt might, therefore, not have been an oxidation product of the acid whose cinchonine salt we had in hand. In other words, it remained to be proved that the cinchonine salt was that of *d*-mannuronic acid. This is shown to be the case in the present paper. The problem as to whether or not there are other uronic acids present in the algin remains for the future.

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[1] Nelson and Cretcher, THIS JOURNAL, **51**, 1914 (1929).

Experimental Part

Preparation of the Lactone.—Five grams of cinchonine salt was dissolved in 125 cc. of water. The cinchonine was precipitated by addition of the calculated amount of (thrice recrystallized) barium hydroxide solution. A drop of phenolphthalein was added to the filtered solution and the pink color discharged by a few drops of dilute sulfuric acid. The solution was filtered through "Nuchar" and evaporated under reduced pressure to a few cc. The barium salt was then precipitated by the addition of 95% alcohol. The salt was dissolved in water, evaporated to a small volume and again precipitated with alcohol. Barium was removed with sulfuric acid. The solution, after filtering through "Nuchar," was again evaporated under reduced pressure to a thick sirup which was placed in a vacuum desiccator for nineteen days over phosphorus pentoxide. During the drying period the material slowly crystallized. It was extracted twice with 5-cc. portions of hot glacial acetic acid and filtered. There was a considerable residue insoluble in acetic acid which proved to be inorganic. Crystallization of the lactone occurred as soon as the solution was cool. After standing for several hours, the mother liquor was decanted and the crystals were washed twice with absolute alcohol and ether. The melting point was 136–138°. After twice recrystallizing from glacial acetic acid, the melting point was constant at 140–141°. On further heating effervescence took place at 153–155°.

Anal. Calcd. for $C_6H_8O_6$: C, 40.90; H, 4.58. Found: C, 40.73, 41.04; H, 4.64, 4.59 (micro). 5.109 mg. required 2.35 cc. of 0.01263 N NaOH. Calcd. neutralization equivalent: 176. Found: 172. 0.0551 g. in 3.017 cc. of aqueous solution gave α $+1.64°$ in a 1-dm. tube; $[\alpha]_D^{25}$ $+89.8°$. There was no mutarotation in forty-six hours. Uronic acid CO_2: 0.1829 g. of sample gave 0.0462 g. of CO_2. Calcd. for $C_6H_8O_6$: CO_2, 25.0. Found: CO_2, 25.26.

The lactone was titrated for aldehyde according to the method of Willstätter and Schudel.[2] A large excess of iodine over the amount theoretically required for an aldehyde of molecular weight 176 was required. Much of the iodine was consumed in the production of iodoform. This is in harmony with our observation that mannosaccharic acid was easily oxidized by cold alkaline iodine with formation of much iodoform. The study of this reaction and the identification of its products are now under way.

Identification of the Lactone.—0.250 g. of lactone and 0.924 g. of barium benzoate[3] were dissolved in 30 cc. of water; 0.1 cc. of bromine was added and the solution allowed to stand in the dark for forty-eight hours. The solution was filtered to remove the precipitated benzoic acid and the excess bromine was evaporated by passage of a stream of air. The solution was twice extracted with chloroform and heated for thirty minutes with an excess of barium carbonate. After filtering, the solution was evaporated to a few cc. under reduced pressure. A granular precipitate of the barium salt formed during evaporation. The precipitation was completed by the addition of several volumes of alcohol. The salt was dissolved in hot water and again evaporated and treated with alcohol. After filtering and washing with alcohol, the barium was removed with sulfuric acid, the solution filtered through decolorizing carbon and evaporated, *in vacuo,* to a sirup. Crystallization was induced by seeding with a crystal of mannosaccharic lactone. The partially crystalline sirup was dried for twenty-four hours in a vacuum desiccator over phosphorus pentoxide. The material was twice extracted with about 5-cc. portions of hot glacial acetic acid and filtered. On cooling the product separated in crystalline condition. Again filtered, washed with alcohol and ether and dried, the compound melted at 182–184° with decomposition.

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[2] Willstätter and Schudel, *Ber.*, **51,** 780 (1918).

[3] Hudson and Isbell, THIS JOURNAL, **51,** 2225 (1929).

A sample of pure mannosaccharic lactone melted at 182–183° when heated at the same rate and there was no change in the mixed melting point.

Optical rotation.—0.0360 g. in 3.017 cc. of aqueous solution rotated +2.38° in a 1-dm. tube: $[\alpha]^{20}_{D}$ +199.5°. The sample of *d*-mannosaccharic dilactone prepared in this Laboratory had $[\alpha]^{23}_{D}$ +199.8°. Titration with alkali: 0.0102 g. required 2.01 cc. of 0.0590 *N* NaOH. Neutralization equivalent, calcd.: 87. Found: 86.

The Diamide.—The solution which had been used for determination of the optical activity was evaporated to dryness under reduced pressure and several drops of concd. ammonium hydroxide was added. After several hours a white crystalline compound was deposited. It melted at 189° and after mixing with pure *d*-mannosaccharic diamide the melting point was unchanged.

Summary

A hitherto unknown aldehyde sugar acid—*d*-mannuronic—has been isolated, in the form of its lactone, from the hydrolysis product of the algin in the *Macrocystis pyrifera*.

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[CONTRIBUTION NO. 189 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

THE NITRATION OF ABIETIC ACID AND THE STUDY OF SOME OF ITS NITROGEN DERIVATIVES[1]

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A number of investigators have studied the effect of nitric acid, nitrous acid and nitrogen oxides on more or less purified mixtures of rosin acids. Easterfield[2] reported that nitro derivatives are obtained when abietic acid is treated with nitric acid in glacial acetic acid solution, but gave no experimental data. Johansson[3] first reported a crystalline nitro derivative of abietic acid. This was obtained in 15% yield by the action of fuming nitric acid at a low temperature on an abietic acid of m. p. 155–168° and $[\alpha]_D$ −28.6°. This, a dinitro compound, $C_{20}H_{28}N_2O_6$, m. p. 178–184° and $[\alpha]_D$ +44.25°, was sensitive to light and was easily esterified. Aschan and Virtanen[4] duplicated the work of Johansson on pinabietic acid and obtained the same product. They concluded that Johansson's abietic acid was in reality pinabietic acid.

Dubourg[5] also attempted, unsuccessfully, to duplicate the work of Johansson on an abietic acid $[\alpha]_D$ −100°. Dubourg, however, succeeded

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[1] This paper is an abstract of a thesis presented to the Graduate School of the University of Pittsburgh by L. A. Goldblatt in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

[2] T. H. Easterfield and George Bagley, *J. Chem. Soc.*, **85**, 1238 (1904).

[3] M. D. Johansson, *Arkiv. Kemi. Min. Geol.*, **6**, No. 19, July (1917), and *Mon. sci.*, **88**, 73 (1921).

[4] Ossian Aschan and A. I. Virtanen, *Ann.*, **424**, 150 (1921).

[5] J. Dubourg (a) *Bull. inst. pin.*, No. **41**, 241 (1927), and (b) No. **59**, 138 (1929).