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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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).

in isolating several white crystalline nitro derivatives of abietic acid. A dinitro derivative, $C_{19}H_{26}N_2O_6$, m. p. 162–165° and $[\alpha]_D$ $-115°$, was obtained by the action of concentrated nitric acid on a hot alcohol or acetic acid solution of abietic acid. The maximum yield was 33%. This compound was stable toward light and air, markedly levorotatory and could be esterified only with difficulty. It was, therefore, different from the dinitro compound of Johansson and Aschan and Virtanen. A trinitro compound, $C_{16}H_{17}N_3O_8$, m. p. 156–158° and $[\alpha]_D$ $-136.2°$, was prepared by the action of fuming nitric acid on the dinitro derivative. A different trinitro derivative, $C_{20}H_{23}N_3O_8$, m. p. 177–178° and $[\alpha]_D$ $-95°$, was prepared with a yield of 2–3% by the action of concentrated nitric acid at room temperature on a solution of abietic acid in carbon tetrachloride.

Patents covering the products obtained by the action of nitric acid on rosin or rosin acids have been granted to Fry, Kesler and Arnot,[6] but these patents were entirely concerned with empirical processes.

There has been considerable controversy as to the products obtained by previous investigators from the nitration of abietic acid. Further, only low yields of products were reported and practically nothing was said as to the fate of the remainder of the abietic acid used. It was therefore deemed desirable to make a further study of the nitration of abietic acid. It was also the purpose of this investigation to study certain chemical properties of abietic acid and derivatives such as salts and esters with special reference to nitration and the reduction of nitro bodies produced.

Experimental Part

Nitration of Abietic Acid.—Twenty-four experiments were conducted to observe the effect of nitric acid on abietic acid or sodium tetra-abietate, prepared according to the method of Kesler,[7] dissolved in alcohol. The effects of concentration of abietic acid, concentration of nitric acid, stirring, temperature and time of reaction were studied. In general, two products were obtained, a white crystalline dinitro derivative and a yellow uncrystallizable nitrogen-containing product. The formation of the white dinitro compound was accompanied by a vigorous effervescence and frothing and, in general, was favored by a high temperature, a short time of reaction and an excess of nitric acid. A maximum yield of 40% of the white dinitro compound was obtained in this series of experiments. A yield of 50% was obtained in an experiment in which the combined mother liquor and wash alcohol from one nitration was used as the solvent for a second nitration.

A Typical Experiment.—One hundred grams of abietic acid, m. p. 166° and $[\alpha]_D^{20}$ $-67°$, and 200 cc. of 95% ethyl alcohol were placed in a 5-liter round-bottomed pyrex flask. The mixture was heated to boiling on a water-bath. When solution was effected,

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[6] George Fry, U. S. 754,298, March 8, 1904; J. J. Kesler, U. S. 922,596, May 25, 1909; Robert Arnot, German Patent 337,954, June 7, 1921; French Patent 520,984, July 5, 1921.

[7] C. C. Kesler, Alexander Lowy and W. F. Faragher, This Journal, **49**, 2898 (1927).

fifteen 5-cc. portions of nitric acid (sp. gr. 1.42) were added at half-minute intervals. The last 5 cc. was added in 0.5-cc. portions at half-minute intervals, and was allowed to run down the side of the flask. This procedure is necessary in order to start a localized reaction. The solution was colored a deep brownish-black at this stage. A violent frothing accompanied by the evolution of a small amount of nitrogen oxides, carbon dioxide and acetaldehyde commenced when the last portion was added. The flask was quickly removed from the water-bath and the upper surface cooled by means of cold wet cloths to prevent expulsion of the liquid by the violent frothing. The reaction soon subsided and a clear orange colored liquid resulted.

On cooling, needle-like crystals gradually formed throughout the entire liquid. The crystals were filtered by suction and washed with 150 cc. of alcohol. They were recrystallized from alcohol and dried in vacuo over anhydrous calcium chloride. Twenty g. of a white crystalline material, discussed as the white dinitro compound, m. p. 170–171° and $[\alpha]_D^{20}$ $-118°$, was thus obtained. (All melting points have been corrected. The rate of heating for the last 20° was 2–3° per minute. The rotation in this case was measured on a 0.6% solution in 95% ethyl alcohol.) The combined filtrate and wash liquor was placed in an ice-box overnight. The additional crystalline deposit was filtered and treated like the above-described first crop. In this way an additional 10 g. of the white crystals was obtained. In order to get a second crop, this cooling should not be too intense as an orange oily product separates when this solution is cooled to −10°.

The orange colored filtrate was then poured with vigorous stirring into 3 liters of water acidulated with 100 cc. of concentrated hydrochloric acid. An orange-yellow amorphous precipitate was thus obtained; (when the water was not previously acidulated a gelatinous precipitate, difficult to filter, was formed). This product was filtered by suction and washed free of chlorides with about 10 liters of water. When dried *in vacuo* over calcium chloride, 75 g. of a yellow nitrogen-containing product (discussed as the yellow nitrogen-containing product) was obtained.

Neither the white dinitro compound nor the yellow product were obtained when an alcoholic solution of abietic acid was treated with ethyl nitrate, used alone or with a little nitric acid, as the nitrating agent.

Other Nitration Experiments.—Seventeen experiments were conducted to observe the effect of various amounts of nitric acid on abietic acid in acetic acid solution at temperatures ranging from 25–120°. Very little reaction took place at low temperatures and there was no frothing below 90°. Above 90° frothing occurred, the reaction mixture became orange-red in color and the yellow nitrogen-containing product was obtained. When acetic acid was used as a solvent, only a small quantity of the white crystalline dinitro acid was obtained. The maximum yield of this compound, 4%, was obtained in an experiment in which 4 cc. of concentrated nitric acid was added in 0.5-cc. portions at half-minute intervals to a solution of 10 g. of abietic acid in 25 cc. of acetic acid at a temperature of 90°.

Several experiments were carried out on the nitration of abietic acid dissolved in benzene, nitrobenzene, carbon tetrachloride and 1,4-dioxan. The white dinitro compound was not obtained in any of these experiments. The use of concentrated nitric acid and elevated temperature resulted in the formation of the yellow nitrogen-containing product.

A number of experiments were conducted in which abietic acid or sodium tetra-abietate was treated directly with nitric acid. Oxidation occurred and no crystalline nitro derivatives of abietic acid were isolated. The results obtained were invariably the yellow uncrystallizable nitrogen-containing material.

The White Dinitro Compound.—The rate of heating affects the melting point of this compound. After two recrystallizations from alcohol, the following melting points were observed. Rate of heating above 140°: 1° per minute, m. p. 163.8–164.2°; 1.5° per minute, m. p. 165.9–166.2°; 2.5° per minute, m. p. 171.2–171.4°. Successive recrystallizations from alcohol, ether, acetic acid and acetone did not appreciably alter the melting points taken at corresponding rates.

The analytical data presented by Dubourg[5a] are quite inconclusive. Since the melting point was higher and since Dubourg reported the loss of a methyl group, this compound was analyzed. Analysis substantiated the formula $C_{19}H_{26}N_2O_6$ proposed by Dubourg.

Anal. Calcd. for $C_{19}H_{26}N_2O_6$ (without CH_3): C, 60.28; H, 6.93; N, 7.41, neutral equivalent, 378.2. Calcd. for $C_{20}H_{28}N_2O_6$ (with CH_3): C, 61.19; H, 7.19; N, 7.16; neutral equivalent, 392.2. Found: C, 59.94, 59.45; H, 7.30, 7.21; N, 7.57, 7.68, 7.33, 7.63, 7.67; neutral equivalent, 374.5, 367.4, 373.7.

The sodium salt was precipitated by adding an excess of 30% aqueous sodium hydroxide to an alcoholic solution of the dinitro compound. After washing with alcohol and drying in vacuo over calcium chloride, it was analyzed as the sulfate.

Anal. Calcd. for $C_{19}H_{25}N_2O_6Na$ (without CH_3): Na, 5.75. Calcd. for $C_{20}H_{27}N_2O_6$-Na (with CH_3): Na, 5.56. Found: Na, 5.56, 5.78, 5.71.

The ethyl ester, m. p. 157.5–157.8°, was prepared by refluxing an alcoholic suspension of the sodium salt with diethyl sulfate. This compound was also prepared by the action of nitric acid on an alcoholic solution of ethyl abietate,[8] b. p. 195–200° (4 mm.).

It is quite difficult to saponify this ester. Analysis indicated the formula $C_{21}H_{30}N_2O_6$ for this compound and thus further substantiated the formula $C_{19}H_{26}N_2O_6$ for the free acid.

Anal. Calcd. for $C_{21}H_{30}N_2O_6$ (without CH_3): C, 62.04; H, 7.44; N, 6.90. Calcd. for $C_{22}H_{32}N_2O_6$ (with CH_3): C, 62.82; H, 7.67; N, 6.65. Found: C, 61.74, 61.63; H, 7.52, 7.61; N, 7.21, 7.04, 7.17, 7.13, 7.12.

Molecular weight determinations of the white dinitro compound indicate slight association in ethyl acetate solution and considerable association in benzene solution. Calcd. for $C_{19}H_{26}N_2O_6$ (without CH_3): mol. wt., 378.2. Calcd. for $C_{20}H_{28}N_2O_6$ (with CH_3): mol. wt., 392.2. Found: mol. wt., 401.1 (in ethyl acetate); 571.2 (in benzene).

Saponification experiments indicated that the white dinitro compound is a nitro derivative of abietic acid and not a nitrate. It was reduced by means of zinc dust and acetic acid, zinc dust and hydrochloric acid in 50% ethyl alcohol and alkaline sodium "hydrosulfite," $Na_2S_2O_4$. It was also reduced catalytically in ethyl acetate solution with a platinum oxide catalyst, $PtO_2 \cdot H_2O$, prepared according to the method of Adams and Shriner.[9]

Nitrogen oxides were evolved during the reduction in acid solution. Ammonia was evolved during the reduction in alkaline solution. A white solid melting at 171.5–172° was precipitated in 80% yield from the ethyl acetate solution during the catalytic reduction. One mole of the white dinitro compound absorbed 1.74 moles of hydrogen during the reduction. The reduction product evolved ammonia when dissolved in hot alcohol or when treated with cold dilute aqueous alkali.

The Yellow Nitrogen-Containing Product.—The yellow nitrogen-containing product did not have a definite melting point but decomposed above 100°. A 0.5% solution in alcohol gave $[\alpha]^{20}_{D}$ −36°. This product was only slightly soluble in chloroform, carbon tetrachloride and petroleum ether. Attempts to separate components of this material

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[8] Supplied by the Hercules Powder Company.

[9] Roger Adams and R. L. Shriner, This Journal, **45**, 2171 (1923).

and to secure crystalline products by the use of a number of solvents, mixtures of solvents and partial precipitation of metallic salts were unsuccessful. This product dissolved in cold aqueous sodium hydroxide, potassium hydroxide and ammonium hydroxide, imparting a deep red color to the solution. Abietic acid dissolved in these reagents forming colorless solutions. The respective products were reprecipitated by bubbling carbon dioxide through the solution. The analytical data show this to be a nitrogen-containing hydroxylated acid.

Anal. Found: C, 63.76, 63.60, 63.27, H, 7.83; N, 6.74, 6.46, 6.70. Neutral equivalent, 365.5, 367.7. Acetyl chloride indicated the presence of 0.84 OH per neutral equivalent.

The red alkaline aqueous solution of this yellow nitrogen-containing product completely absorbed oxygen from air; 300 cc. of a 3% alkaline solution absorbed 20 cc. of oxygen in fifteen minutes; 1.8 g. dissolved in 100 cc. of 1% aqueous sodium hydroxide absorbed 92 cc. of oxygen in the course of three days. The alkaline solution froths or lathers quite readily.

The yellow product was reduced in the same manner as the white dinitro compound. Nitrogen oxides were evolved during reduction in acid media and ammonia was evolved during reduction in alkaline media. The evolution of ammonia when the catalytic reduction product was made alkaline indicated the reduction of a nitro group. No crystalline reduction products of the yellow nitrogen-containing material could be obtained. Analysis of the brown solid obtained by pouring the zinc–acetic acid reduction product into water further indicated the loss of nitrogen from this product during the reduction.

Anal. Found: (before reduction): N, 6.74, 6.46; (after reduction): N, 3.54, 3.64.

A light yellow sodium salt was precipitated from acetone solution when aqueous sodium hydroxide was added drop by drop. Attempts at esterification of the sodium salt of the yellow product with dimethyl or diethyl sulfate resulted only in uncrystallizable tars.

Summary

1. A study of the conditions of nitration of abietic acid and some of its derivatives has been made.

2. Two main products were obtained: a white crystalline dinitro acid, $C_{19}H_{26}N_2O_6$ (substantiating Dubourg's results), m. p. 171.2–171.4° (Dubourg reported a m. p. of 162–165°) and a yellow amorphous nitrogen-containing product, decomposing above 100°. The latter is a hydroxylated nitro derivative of abietic acid while the former is not. The properties of these products have been studied.

3. The alkaline solution of the yellow nitrogen-containing product readily absorbs oxygen.

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