formation of the dibromo derivative, which could not be removed from the monobromo derivative by recrystallization. Analysis proved that the pure compound had been separated. The crystalline compound is easily soluble in ordinary solvents except petroleum ether and water. It is slightly bitter and was kept for many months without decomposition in a desiccator over sodium hydroxide in the ice box.

Rotation.—Subs., 0.6101: $\alpha = +17.640°$; $[\alpha]^{20}_{D} = +180.54°$. Recrystallization. Subs., 0.3872: $\alpha = +11.177°$; $[\alpha]^{20}_{D} = +180.24°$.

Other preparations gave values near +180.10°, which is taken as the specific rotation of the pure substance.

Anal. Subs., 0.1718: CO_2, 0.2827; H_2O, 0.0808. Subs., 0.2177: AgBr, 0.0581. Calcd. for $C_{26}H_{35}O_{17}Br$: C, 44.62 H, 5.05; Br, 11.43. Found: C, 44.88; H, 5.26; Br, 11.36.

Summary

The pure crystalline fluoro, chloro and bromo derivatives of acetylated melibiose and maltose have been prepared and described. The specific rotational values of these α-biose derivatives show an agreement with the atomic dimension relationship of the monose sugars, whereas the values for the halogen derivatives of the β-bioses, investigated before, agree with this relationship only by excluding the values for the fluoro derivatives. An explanation of this behavior is obtained by model studies, which show that the *direction* of the β-valence allows the constituting monoses to face each other, with a resulting selective influence, whereas the direction of the α-valence does not allow this position. The new (more detailed) structure formula for cellobiose suggests a structure formula for cellulose. As compared with formulas heretofore suggested this new formula gives a better interpretation of the chemical and physical properties of cellulose.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS, NORTHWESTERN UNIVERSITY]

THE MERCURATION OF NAPHTHALIC ACIDS

BY G. J. LEUCK AND R. P. PERKINS WITH FRANK C. WHITMORE

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While the replacement by mercury of one of the carboxyl groups in phthalic acid has long been known,[1] the effect of changes in structure on this reaction has not been studied extensively.

In the present study naphthalic acid, 3-nitronaphthalic acid and 4-nitronaphthalic acid have been submitted to the reaction of Pesci. In each case one of the carboxyl groups was replaced by mercury. Naphthalic acid gave anhydro-8-hydroxymercuri-1-naphthoic acid. With 3-nitronaphthalic acid the carboxyl in the 8-position was replaced more than that in the 1-position. With 4-nitronaphthalic acid the replacement was almost entirely in the 8-position, only a small amount of replacement taking

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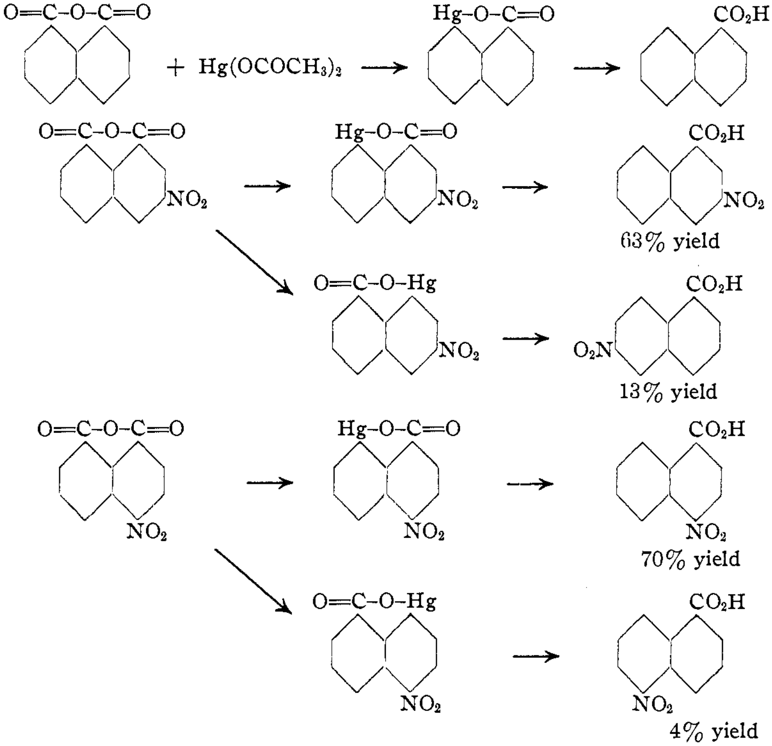
[1] Pesci, *Atti. accad. Lincei,* [5] **10,** I, 362 (1901).

place in the 1-position. In each case the products were identified by replacement of the mercury by hydrogen by means of hydrochloric acid.



In addition to the theoretical interest in these reactions they offer the best methods of preparing 3-nitro-1-naphthoic acid and 4-nitro-1-naphthoic acid in a high state of purity and in good yields.

Experimental Part

The Mercuration of Naphthalic Acid.—Acenaphthene was oxidized by sodium dichromate in glacial acetic acid.[2] From 100 g. of 75% acenaphthene was obtained 90 g. of purified naphthalic acid (1,8-naphthalenedicarboxylic acid), m. p. 270–271° (85% yield).

A filtered solution of 50.5 g. of naphthalic acid in 1.2 liters of water and 31 g. of sodium hydroxide was mixed with a solution of 55 g. of mercuric oxide in 150 cc. of water and 40 cc. of glacial acetic acid. A slight excess of acetic acid was added and the mixture was refluxed for ninety-eight hours. No more carbon dioxide was evolved and a test sample of the mixture dissolved in sodium hydroxide. The solution gave no metallic mercury when tested with a clean copper wire. The precipitate which had formed was collected on a filter and washed. It was dried at 105°. The yield of **anhydro-8-hydroxymercuri-1-naphthoic acid** was 84.6 g. (97.6% of the theoretical).

Anal. Calcd. for $C_{11}H_6O_2Hg$: Hg, 54.1. Found: Hg, 52.2, 53.7, 53.4.

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[2] Graebe and Gfeller, *Ber.*, **25**, 652 (1892).

Attempts to purify the anhydro compound were unsuccessful. It is insoluble in organic solvents. Acidification of its alkaline solution gives a gelatinous precipitate which is very difficult to wash and dry.

Sodium 8-hydroxymercuri-1-naphthoate was obtained by evaporating a strongly alkaline solution of the anhydro compound until large white crystals separated on slowly cooling. The crystals were washed with alcohol and dried at 50°.

Anal. Calcd. for $C_{11}H_7O_3HgNa$: Hg, 48.8. Found: Hg, 48.1, 48.2.

The salt is readily soluble in water containing a little sodium hydroxide. It is readily hydrolyzed by pure water.

A hot solution of 46.5 g. of the sodium salt in 500 cc. of water was treated with 200 cc. of concd. hydrochloric acid and boiled for three hours. The **1-naphthoic acid** obtained was crystallized from hot alcohol; m. p. 162°; wt. 17 g. (87% yield). 1-Naphthoic acid was also prepared from the anhydro compound and hydrochloric acid; yield, 90%.

The Mercuration of 3-Nitronaphthalic Acid.—The anhydride was prepared from naphthalic acid in concd. sulfuric acid solution and solid potassium nitrate at 10–15°.[3] The product after removing impurities with hot toluene (4 cc. per g.) melted at 247–250°; yield, 300 g. from 298 g. of naphthalic anhydride (81% of the theoretical). The pure anhydride was obtained by crystallization from nitrobenzene (225 cc. per 100 g.) or glacial acetic acid (3 liters per 100 g.); m. p. 252–253°.

The anhydride was mercurated in the usual way. From 304 g. of 3-nitronaphthalic anhydride was obtained 505 g. of a mixture of anhydro-3-nitro-8-hydroxymercuri-1-naphthoic acid and the corresponding 6-nitro compound (97% of the theoretical). It is a creamy white powder.

Anal. Calcd. for $C_{11}H_5O_4NHg$: Hg, 48.2. Found: Hg, 48.3.

No way was found for purifying the product.

Sodium 3-nitro-8-hydroxymercuri-1-naphthoate was prepared by dissolving the crude mercurated product in a slight excess of sodium hydroxide and evaporating until crystals separated on cooling. The salt is much less soluble than the corresponding naphthoic compound. It forms large yellow crystals.

Anal. Calcd. for $C_{11}H_6O_5NHgNa$: Hg, 44.0. Found: Hg, 43.3, 43.8.

Sodium 8-Mercuribis-3-nitro-1-naphthoate ("No. 93").—Starting with 480 g. of naphthalic acid, 70 g. of the desired sodium salt was obtained. The conversion of the hydroxymercuri compound to the mercuri*bis* compound was effected by refluxing with an excess of alcoholic sodium iodide. The product was free of iodides.

Anal. Calcd. for $C_{22}H_{10}O_8N_2HgNa_2$: Hg, 29.6. Found: Hg, 28.9.

Structure of the Mercuration Products.—The mixture of mercury compounds obtained from 3-nitronaphthalic acid was treated with hydrochloric acid for two hours. From 200 g. was obtained 103 g. of a light cream-colored powder (98% of the theoretical). This was dissolved in 1.5 liters of hot glacial acetic acid, filtered from a slight residue and cooled. Fine needle crystals separated, m. p. 265.5°; yield, 65.8 g. (63% of amount theoretically obtainable from the mercurated material). This was nearly pure **3-nitro-1-naphthoic acid.** In another run the yield was 60.5 g., m. p. 269–270°. The highest melting point obtained for this acid by repeated crystallization from alcohol was 270.5–271.5°. With smaller runs slightly higher yields were obtained. All the mother liquors were saved for the recovery of 6-nitro-1-naphthoic acid.

Anal. Calcd. for $C_{11}H_7O_4N$: C, 60.8; H, 3.23; N, 6.45. Found: C, 60.5, 60.7; H, 3.09, 3.32; N, 6.39.

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[3] Graebe and Briones, *Ann.*, **327**, 84 (1903).

Ethyl 3-nitro-1-naphthoate was prepared from the acid by thionyl chloride and absolute ethyl alcohol. It formed yellow needles from alcohol and rhombic plates from ethyl acetate, m. p. 87.5–88.5°. The ester did not react with ammonia in water, in alcohol or when fused.

3-Nitro-1-naphthamide was prepared from the acid with thionyl chloride and ammonia, m. p. 264–269°. The amide is difficultly soluble in ethyl alcohol, insoluble in water, difficultly soluble in xylene, slightly soluble in carbon tetrachloride, acetone and benzene, and very soluble in glacial acetic acid. Several crystallizations from ethyl alcohol raised the melting point to 280–280.8°.

Anal. Calcd. for $C_{11}H_8O_3N_2$: N, 12.96. Found: Hg, 12.9.

When 3-nitro-1-naphthamide was treated with sodium hypochlorite or sodium hypobromite, the expected 3-nitro-1-aminonaphthalene was *not* obtained.[4] The products were apparently halogen derivatives of this substance. This behavior was in marked contrast to that of the 6-nitro-1-naphthamide, which gave 6-nitro-1-aminonaphthalene without any complications.

The hydrochloride of 3-amino-1-naphthoic acid was obtained in 90% yield by reducing the nitro compound with sodium hydrosulfite. The preparation of the free amine proved to be very difficult. It was obtained from the hydrochloride in small yields as straw-colored aggregates of needle crystals, m. p. 181–182°.

Anal. (of impure material, m. p. 170–172°). Calcd. for $C_{11}H_9O_2N$: N, 7.49. Found: N, 7.83.

3-Acetamino-1-naphthoic acid was prepared from the amine and acetic anhydride as cream-colored needles, m. p. 254–255°. The hydrochloride was converted into the known[5] 3-hydroxy-1-naphthoic acid by diazotizing at 0° and pouring into boiling 30% copper sulfate solution. The product extracted with ether melted at about 210°. Two crystallizations from water gave yellow needles, m. p. 228–231°. Purification by sublimation raised the melting point to 239–241° (Royle and Schedler give 242–243°). Solutions in ether, in aqueous alcohol and in benzene have a blue-purple fluorescence. It gives a deep red-brown color with ferric chloride.

The acetyl derivative of 3-hydroxy-1-naphthoic acid was prepared in the usual way, m. p. 172° (Royle and Schedler give 169–170°).

The mother liquors from the crystallization of the mixed acids from 200 g. of the mercury product from 3-nitronaphthalic acid were evaporated to dryness on the steam-bath under reduced pressure; wt., 35 g. This material was treated with 250 cc. of absolute alcohol, saturated with dry hydrogen chloride, refluxed for a short time, allowed to stand for several days, cooled and filtered. The product consisted of lumps of white crystals, m. p. 105–107°; wt., 13.7 g. This was fairly pure ethyl **6-nitro-1-naphthoate**. Further crystallization from ethyl alcohol raised the melting point to 111.5–112°. Evaporation of the alcoholic mother liquors gave a mixture of esters of the 3- and 6-nitro compounds which was not further separated.

The ester of 6-nitro-1-naphthoic acid was hydrolyzed to give an acid melting at 207–220°. Several crystallizations from glacial acetic acid raised the melting point to 224–225.5°. Another crystallization from toluene gave the melting point 225–226°. Sublimation gave the highest melting point obtained, 227–227.5°. This was **6-nitro-1-naphthoic acid**.

Anal. Calcd. for $C_{13}H_{11}O_4N$: C, 60.8; H, 3.23; N, 6.45. Found: C, 60.7; H, 3.31; N, 6.66.

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[4] **Veselý and Dvořák**, *Bull. soc. chim.*, [4] **33**, 327 (1923).

[5] Royle and Schedler, *J. Chem. Soc.*, **123**, 1642 (1923).

6-Nitro-1-naphthamide was prepared in the usual way. Two crystallizations from alcohol gave fine cream-colored needles, m. p. 216.5°.

Anal. Calcd. for $C_{10}H_8O_2N$: N, 12.96. Found: N, 13.0.

Treatment with sodium hypochlorite gave **6-nitro-1-aminonaphthalene**, m. p. 172–173° (Veselý and Dvořák, ref. 4, give 167°).

6-Nitro-1-acetaminonaphthalene was prepared, m. p. 237–238° (Veselý and Dvořák give 232–233°).

Reduction of the nitro acid by sodium hydrosulfite in 6 *N* sodium hydroxide gave the known[6] **6-amino-1-naphthoic acid**, m. p. 205.5–206.5° (Harrison and Royle give 203°). An alcoholic solution gives a green fluorescence.

6-Acetamino-1-naphthoic acid was prepared in the usual way. It forms light yellow needles from dilute acetic acid, m. p. 253° (Harrison and Royle give 170–172°).

Mercuration of 4-Nitro-1-Naphthalic Acid.—Acenaphthene was nitrated and the nitro compound was oxidized to give 4-nitro-1-naphthoic anhydride.[7] From 91 g. of 75% acenaphthene was obtained 63 g. of 4-nitro-1-naphthalic anhydride, m. p. 220–224°. Purification through the calcium salt and crystallization from glacial acetic acid raised the melting point to 230°. The anhydride was mercurated in the usual way. The time of refluxing was fifty hours. From 50 g. of the anhydride were obtained 79.7 g. of mercurated product, mainly **anhydro-4-nitro-8-hydroxymercuri-1-naphthoic acid** and a little of the 5-nitro compound.

Anal. Calcd. for $C_{11}H_5O_4NHg$: Hg, 48.2. Found: Hg, 48.4, 48.7.

Treatment of this mixture with hydrochloric acid gave a 95% yield of mixed acids, m. p. 210–218°. Ten g. of the mixed acids on several crystallizations from glacial acetic acid gave 7.1 g. of 4-nitro-1-naphthoic acid, m. p. 225–226°. Repeated attempts to obtain any other acid from the mother liquors failed. The mixed acids were esterified by treatment with thionyl chloride and ethyl alcohol. It was not possible to separate any ester other than the 4-nitro compound.

Ethyl 4-nitro-1-naphthoate and the corresponding **methyl ester** were prepared from the pure acid; m. p. of ethyl ester, 57–58°; methyl ester, 107.5–108.5°.

The mother liquors from a batch of 4-nitro-1-naphthoic acid were evaporated to dryness; wt., 4 g.; m. p. 216–222°. This was converted to the mixed amides by thionyl chloride and ammonia. After repeated fractionation from dilute ethyl alcohol the insoluble end gave 0.6 g. of **5-nitro-1-naphthamide**, m. p. 230–232°.[8] This corresponded to about 4% of the original mixed acids. A known sample of the 5-nitro-1-naphthamide was prepared from 5-nitro-1-naphthoic acid.[9] A sample of this amide melting at 233–235° was mixed with the amide from the mixed acids. The mixture melted at 230–233°. Recrystallized from benzene the amide melts at 235–236°.

Summary

1. Naphthalic, 3-nitronaphthalic and 4-nitronaphthalic acids were treated with mercuric acetate. In each case one carboxyl was replaced by mercury. With the nitro acids the replacement was *mainly* in the ring not containing the nitro group.

2. The following mercury compounds were prepared: anhydro-8-

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[6] Harrison and Royle, *J. Chem. Soc.*, **129**, 87 (1926).

[7] Graebe and Briones, *Ann.*, **327**, 80 (1903).

[8] 4-Nitro-1-naphthamide melts at 218°. Friedlaender and Weisberg, *Ber.*, **28**, 1841 (1895).

[9] Ekstrand, *J. prakt. Chem.*, [2] **38**, 276 (1888).

hydroxymercuri-1-naphthoic acid, its sodium salt, sodium 3-nitro-8-hydroxymercuri-1-naphthoate, sodium 8-mercuri*bis*-3-nitro-1-naphthoate and anhydro-4-nitro-8-hydroxymercuri-1-naphthoic acid.

3. Other compounds were prepared, as follows: 3-nitro-1-naphthoic acid, its ethyl ester, its amide, 3-amino-1-naphthoic acid, its acetyl derivative, 6-nitro-1-naphthoic acid, its ethyl ester, its amide, 5-nitro-1-naphthamide.

4. Satisfactory preparative methods were developed for 3-nitro-1-naphthoic acid and 4-nitro-1-naphthoic acid.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

CALYCANTHINE. I. THE ISOLATION OF CALYCANTHINE FROM MERATIA PRAECOX

BY RICHARD H. F. MANSKE[1]

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The first chemical investigation of the alkaloid, calycanthine, was made by Gordin.[2] He obtained it from *Calycanthus glaucus, Willd.*, and described a convenient procedure for its isolation. In later papers by the same author[3] we are informed that a second lot of seeds, presumably identical with the first, yielded only an isomeric base, namely, isocalycanthine.

Recently a contribution by Späth and Stroh[4] elucidated some obscure points in Gordin's work and established the empirical formula $C_{22}H_{28}N_4$, although the present author is of the belief that $C_{22}H_{26}N_4$ is not entirely excluded.

It was decided to subject the alkaloid to a more rigorous examination and, if possible, to elucidate the relation between calycanthine and isocalycanthine, if indeed the latter has an existence. It may be mentioned that botanists do not appear to be in complete accord in regard to the nomenclature of the various species of *Calycanthus*, but it may be taken for granted that *Calycanthus floridus L.*, and *Calycanthus fertilis, Walt.* (*C. glaucus, Willd.*) are two distinct species. From the former the author has isolated about 1.2% of an alkaloid which appears to be identical in all respects with Gordin's calycanthine and also with the base examined by Späth and Stroh.[4] No evidence of the presence of isocalycanthine has been forthcoming although other bases appear to be present in small amounts. The possibility is not excluded that Gordin's second lot of seeds in reality consisted of *C. fertilis*, whereas the first was *C. floridus*. When the former seeds become available an attempt will be made to determine this point.

[1] Holder of the Eli Lilly Company Research Fellowship at Yale University, 1927–1928–1929.

[2] Gordin, THIS JOURNAL, **27**, 144, 1418 (1905).

[3] Gordin, *ibid.*, **31**, 1305 (1909); **33**, 1626 (1911).

[4] Späth and Stroh, *Ber.*, **58**, 2131 (1925).