the acute angle of the rhombs, and the acute bisectrix inclined to the principal plane of the crystals; optically positive.

Nitrate.—Recrystallized from water, the crystals are in the form of oblique prisms with beveled edges, the ends truncated by a pinacoid at about 70° to their axis. The double refraction is strong, with oblique extinction exhibited by all views of the prisms. The extinction angle varies, depending on the orientation, but the maximum is about 35°; biaxial interference figure; 2V large, with plane of optic axis obliquely transverse of the crystals, optically positive,

Picrate.—Spherulites, crosses, dendrites, fine needles, prisms, and small tablets, six-sided in outline and having terminal angles of about 95° may be seen. Double refraction is very strong, with symmetrical extinction; biaxial interference figure; 2V large, with plane of the optic axis transverse of the crystals, optically negative.

Chloroplatinate.—The golden-yellow crystals are sparingly soluble in water and when precipitated show a marked tendency to form a supersaturated solution. The crystals are oblique bi-pyramids, with basal and clino-pinacoids. They show strong double refraction and all views show oblique extinction; biaxial; 2V large; probably optically positive.

Summary

The reaction between methyl-isothiourea sulfate and aniline resulted in the formation of a product consisting of α-phenylguanidine sulfate and aniline sulfate. Pure α-phenylguanidine and a number of its salts were prepared by first converting the α-phenylguanidine sulfate in the crude product to the carbonate. Certain physical and chemical properties of these substances have been described.

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MERCURATION OF RESORCINOL AND SOME ALKYLRESORCINOLS

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No trimercurated derivative of resorcinol has been described in the literature and no work has been published on the mercuation of the alkylresorcinols. Dimroth has prepared a chloromercuriresorcinol and a dichloromercuriresorcinol.[1] Leys has prepared a yellow mercury resorcinol compound to which he gives the formula $HgO_2{=}C_6H_3.HgOAc$.[2] Kharasch and Chalkley[3] have examined the reactivity of acetoxymercurire-

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[1] Dimroth, *Ber.*, **35**, 2865 (1902).

[2] Leys, *J. pharm. chim.*, (6) **21**, 1388 (1905).

[3] Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., Inc., New York, 1921, p. 59.

sorcinol and diacetoxymercuriresorcinol dimethyl ether with ammonium sulfide. Raiziss and Prouskouriakoff[4] have prepared 4-acetoxy- and 4-chloromercuri-2-nitroresorcinol.

Regarding the relation between bactericidal power and weight of the side chain, the work of Johnson and Lane[5] and, more recently, the work of Leonard[6] have shown that the disinfectant power of the alkylresorcinols varies directly with the weight of the side chain, up to and including the hexyl group. Henry and Sharp[7] have mercurated some alkylphenols, and in their work on the bactericidal action of mercury compounds[8] it is shown that the monomercurated *p-tert.*-butylphenol apparently is less effective than the corresponding mono-mercurated *p-iso*-amylphenol.

Because it was thought that the mercurated alkylresorcinols might prove to be good bactericidal agents, and also that the study of the effect of the weight of the side chain in these compounds would prove interesting,[9] some mercurated derivatives of ethyl- and hexylresorcinol have been prepared. Hexylresorcinol has been used because of its high phenol coefficient. Ethylresorcinol has been chosen for comparison because it is probably the easiest and cheapest alkylresorcinol to prepare. Incidentally, a trimercurated derivative of resorcinol has been prepared.

The formulas given are only tentative ones. No attempt has been made to determine the position of the mercury groups because very little information, and mostly none at all, concerning the corresponding iodine derivatives is reported in the literature.[10] It is almost certain, however, that the mercury groups are in ortho and para positions, that is, in positions 2 and 6, to the phenolic hydroxyl groups in the dimercurated alkylresorcinols, and in either one of these two positions in the monomercurated alkylresorcinols. An orientation of the mercury meta to phenolic hydroxyl is entirely improbable.[11]

Ethyl- and hexylresorcinol readily react with two molecular proportions of mercuric acetate dissolved in hot alcohol to give practically quantitative yields of the dimercurated derivatives. There is a complete removal of mercuric ion, as shown by the fact that the filtrates give no precipitate with ammonium sulfide solution. From a determination of the mercury and acetate contents and also the yields obtained, it is believed that one mercury group is an acetoxymercuri group, while the remaining mercury

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[4] Raiziss and Prouskouriakoff, THIS JOURNAL, **44**, 787 (1922).

[5] Johnson and Lane, *ibid.*, **43**, 348 (1921).

[6] Leonard, *J. Urol.*, **12**, 585 (1924).

[7] Henry and Sharp, *J. Chem. Soc.*, **1926**, 2432.

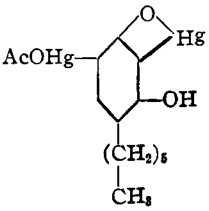
[8] Henry, Sharp and Brown, *Biochem. J.*, 19, 513 (1925).

[9] The bacteriological part of this work is now proceeding.

[10] It is the aim of the author to carry out the preparation of these derivatives in a later piece of work.

[11] Kharasch, THIS JOURNAL, **43**, 1203 (1921).

group is an anhydride group formed by the elimination of acetic acid between the phenolic hydroxyl and the acetoxymercuri group ortho to it. It is also believed that the formation of the anhydride takes place with the mercury in position 2, that is, with the mercury which is between the two phenolic hydroxyls. A suggested structure for the dimercurated hexylresorcinol would be Formula I.



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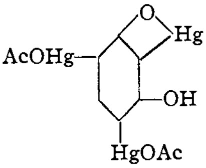
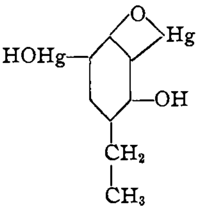


II



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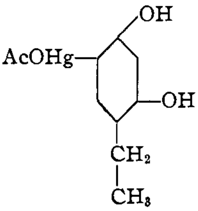

IV

The dimercurated alkylresorcinols prepared by the action of the alkylresorcinols on an alcoholic mercuric acetate solution are insoluble in the ordinary organic solvents, and therefore cannot be purified by crystallization. However, they usually separate in a pure state if care is taken to work with pure starting materials.

The monomercurated alkylresorcinols are prepared by adding one molecular proportion of dry mercuric acetate to two molecular proportions of the alkylresorcinol dissolved in a very small amount of hot glacial acetic acid. The compounds formed in this way are mono-acetoxymercurialkylresorcinols. They, as well as the monochloromercuri compounds, are difficult to obtain in a pure state from solvents because of their tendency to precipitate as yellow, insoluble solids. The latter are probably due to the formation of anhydro monomercurated compounds.

Resorcinol readily forms a trimercurated derivative when one molecular proportion of resorcinol is added to a hot solution of three molecular proportions of mercuric acetate in alcohol. If the proposed formula is correct, the yield is a quantitative one. In this case, too, there is a complete removal of mercuric ion from solution. The suggested formula for this compound is II.

Experimental Part

Mercuration of Alkylresorcinols

Ethylresorcinol.—The ethylresorcinol used was prepared by the method of Johnson and Hodge.[12] One and four-tenths g. (0.01 mole) of ethylresorcinol dissolved in 10 cc. of alcohol was added to a boiling solution of 6.37 g. (0.02 mole) of mercuric acetate dissolved in 50 cc. of alcohol and 5 cc. of glacial acetic acid. Almost immediately a bright yellow solid separated and care was taken to stop heating as soon as the precipitate appeared, due to the violent "bumping" which always occurred. The reaction mixture was allowed to stand for about twelve hours. The mercurated ethylresorcinol

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[12] Johnson and Hodge, THIS JOURNAL, **35**, 1014 (1913).

was filtered off by suction and washed with hot alcohol. It was air dried and then dried *in vacuo* over sulfuric acid. The yield was 5.80 g. or 97%. The compound is insoluble in all ordinary organic solvents but is soluble in a solution of sodium hydroxide. It darkens on exposure to light and when heated at 180° it darkens but does not melt at 300°.

Anal.[13] Calcd. for $C_{10}H_{10}O_4Hg_2$: Hg, 67.40. Found: Hg, 67.34, 67.47, 67.04. 66.85.

On steam distillation, after decomposition by phosphoric acid, it yields 10.20% of acetic acid ($C_{10}H_{10}O_4Hg_2$ requires 10.08% of acetic acid). These results indicate that the compound is an anhydromercuri-acetoxymercuri-ethylresorcinol.

The above mercury compound was converted into the dichlorodimercuri-ethylresorcinol by the addition of hydrochloric acid to a suspension (it was necessary to add a few drops of alcohol to cause wetting) of the former in water. It was also necessary to stir vigorously during the addition of hydrochloric acid to prevent a localized high concentration of hydrochloric acid, which tends to break the carbon–mercury bond. The dichloro compound is a white solid and can be crystallized from alcohol. From this solvent it also tends to separate as a yellow solid which is probably an anhydromercuri derivative. The dichlorodimercuri-ethylresorcinol decomposes at 207–209° (corrected).

Anal. Calcd. for $C_8H_8O_2Cl_2Hg_2$: Hg, 65.96. Found: Hg, 65.82, 65.74.

When carbon dioxide was bubbled through a sodium hydroxide solution of the anhydromercuri-acetoxymercuri-ethylresorcinol, a gelatinous precipitate was formed. This was washed repeatedly with water by decantation, then filtered off by suction and finally dried at 100° for two hours. It was obtained as a dark brown solid. The analysis indicates an anhydromercuri-hydroxymercuri-ethylresorcinol, of which the probable structure is Formula III.

Anal. Calcd. for $C_8H_8O_3Hg_2$: Hg, 72.52. Found: Hg, 72.68, 72.56.

In order to obtain a monomercurated ethylresorcinol, one mole of mercuric acetate was added, with heating and stirring, to two moles of ethylresorcinol dissolved in a very small amount of glacial acetic acid. While still hot the solution was poured into water; thereupon a white solid mono-acetoxymercuri-ethylresorcinol separated. Or, if the hot solution was poured into a saturated salt solution, a white solid monochloromercuri-ethylresorcinol was formed. In both cases the compounds were crystallized from alcohol. It has been impossible so far to separate either the mono-acetoxy or the monochloro compound into two isomeric substances. Preference is given to position 6, as far as the orientation of the mercury group is concerned. Formula IV is given as the probable structure. The mono-acetoxy derivative melts with charring at 163–164° (corrected).

Anal. of mono-acetoxymercuri-ethylresorcinol. Calcd. for $C_{10}H_{12}O_4Hg$: Hg, 50.57. Found: Hg, 50.32, 50.30.

The monochloro compound melts to a clear liquid at 145–146° (corrected).

Anal. of monochloromercuri-ethylresorcinol. Calcd. for $C_8H_9O_2ClHg$: Hg, 53.76. Found: Hg, 53.50, 54.10.

Hexylresorcinol.—The hexylresorcinol for the work was prepared according to the procedure given by Dohme, Cox and Miller.[14] The mercurated hexylresorcinol

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[13] The analysis was carried out by decomposing the mercury compound with fuming nitric acid in a sealed tube at a temperature of 200°. The inorganic mercury in the resulting solution was then determined as mercuric sulfide.

[14] Dohme, Cox and Miller, THIS JOURNAL, **48**, 1688 (1926).

derivatives were obtained by the method already described for the mercurated ethylresorcinol compounds. In general the properties of these two series of compounds are similar. The anhydromercuri-acetoxymercuri-hexylresorcinol was obtained as a bright yellow solid in a practically quantitative yield. In one case 1.94 g. (0.01 mole) of hexylresorcinol and 6.37 g. (0.02 mole) of mercuric acetate gave 6.30 g. of dimercurated derivative, or a yield of 96%. In another case 5.47 g. of hexylresorcinol and 17.95 g. of mercuric acetate gave a yield of 18.30 g., or 100%.

The compound darkens at 200° and does not melt at 300°. It darkens when exposed to light. It is insoluble in the ordinary organic solvents and is difficultly soluble in a solution of sodium hydroxide.

Anal. Calcd. for $C_{14}H_{18}O_4Hg_2$: Hg, 61.60; acetic acid, 9.21. Found: Hg, 61.27, 61.32, 61.29, 60.90; acetic acid, 9.39, 9.40.

The dichloromercuri-hexylresorcinol is a white solid and can be purified from alcohol, from which it also tends to separate as a yellow, insoluble derivative. This difficulty in purification may account for the low mercury results reported below. It melts at 137–138° (corrected).

Anal. Calcd. for $C_{12}H_{16}O_2Cl_2Hg_2$: Hg, 60.40. Found: Hg, 59.66, 59.70.

A mono-acetoxymercuri-hexylresorcinol was prepared. It was crystallized from alcohol. It forms white crystals and melts, with charring, at 177–178° (corrected).

Anal. Calcd. for $C_{14}H_{20}O_4Hg$: Hg, 44.32. Found: Hg, 44.10, 43.80.

Mercuration of Resorcinol

Trimercurated Derivative of Resorcinol.—A trimercurated derivative of resorcinol was obtained by the addition of 1.10 g. (0.01 mole) of resorcinol dissolved in 10 cc. of alcohol to a hot solution of 9.56 g. (0.03 mole) of mercuric acetate dissolved in 75 cc. of alcohol and 5 cc. of glacial acetic acid. The precipitation of the yellow trimercurated compound was almost immediate. Heating was interrupted as soon as the precipitate appeared. It was allowed to stand for twelve hours, then filtered off by suction and washed with hot alcohol. It was dried *in vacuo* over sulfuric acid. The yield was 8.21 g. or practically 100%. There is a complete removal of mercuric ion from solution. It darkens at 210° and does not melt at 300°. It is insoluble in all of the ordinary organic solvents. It is slightly soluble in a solution of sodium hydroxide.

Anal. Calcd. for $C_{10}H_8O_6Hg_3$: Hg, 72.75; acetic acid, 14.53. Found: Hg, 72.50, 72.20; acetic acid, 14.30, 14.40.

Summary

1. The preparation of some mono- and dimercurated derivatives of ethyl- and hexylresorcinol has been described.

2. The preparation of a trimercurated derivative of resorcinol has been described.

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