represents hydroxy acids of very high molecular weight. The investigation of this material will have to be deferred to a future time.

The Solid Reduced Acids.—The solid reduced acids on recrystallization from acetone were obtained in form of colorless plates and had the properties of stearic acid. The melting point was 68–69° and the molecular weight was 283.7.

The Unsaponifiable Matter.—The unsaponifiable matter from H-37 was a dark-colored viscous mass. The iodine number was 194. On combustion it gave the following values: found, C, 81.63; H, 10.76.

An attempt to hydrogenate the substance with platinum oxide as catalyst failed and no hydrogen was absorbed. Reduction with the Raney nickel catalyst[28] at a pressure of 2000 pounds for four hours also failed to yield a saturated compound.[29] The substance recovered after this treatment had an iodine number of 136.

The unsaponifiable matter from A-12 was a dark-colored thick mass with an iodine number of 226. It was possible to isolate 1.2 mg. of a digitonide from 1.51 g.[30] of this unsaponifiable matter as described in a former paper.[22] The digitonide gave a typical Liebermann–Burchard reaction.

Further investigations of the unsaponifiable matter will be carried out in the future.

The Wax Fractions.—The so-called chloroform-soluble wax has not been studied systematically except that the material extracted from strain H-37 was examined for sterols. As already published[22] the unsaponifiable matter from the wax yielded 2.1 mg. of digitonide corresponding to about 0.5 mg. of sterol.

Summary

A study has been made of the lipids isolated from four recently isolated cultures of the human tubercle bacillus in comparison with a freshly cultivated lot of strain H-37.

Great variation in yields of the different lipid fractions as well as in their chemical constants were found.

The pigment phthiocol occurs in the acetone-soluble fats both in the free and combined state.

Optically active acids similar to or identical with phthioic acid were isolated from the acetone-soluble fats.

The acetone-soluble fats from all the strains contain large proportions of free fatty acids while the neutral esters contain trehalose in place of glycerol.

Minimal traces of sterol-like compounds were detected in the acetone-soluble fats and in the crude chloroform-soluble waxes but the quantities are so small that they can be regarded only as accidental impurities and not as metabolic products of the bacillus.

NEW HAVEN, CONN. RECEIVED FEBRUARY 4, 1936

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[28] L. W. Covert and H. Adkins, THIS JOURNAL, **54**, 4116 (1932).

[29] We are indebted to Dr. J. M. Sprague of this Laboratory for carrying out this reduction.

[30] In the paper published in *Z. physiol. Chem.*, **237**, 40 (1935), through a typographical error the weight of the unsaponifiable matter used in this determination is given as 1.15 g. instead of 1.51 g.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, NO. 132, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Studies in the Diphenic Acid Series. V

BY H. W. UNDERWOOD, JR.,[1] AND GEORGE BARKER

In an earlier paper[2] of this series it was reported that phenoldiphenein, the principal product of the reaction of phenol with diphenic anhydride in the presence of fuming stannic chloride, dissolves in aqueous sodium hydroxide to yield a yellow-colored solution. Phenolphthalein, as is well known, gives a deep red solution under similar circumstances. In order to learn more concerning this remarkable difference between substances of presumably analogous structure,[3] we have prepared tetrabromo-, diiodo-, and dinitrophenoldiphenein, *o*-cresoldiphenein, dibromo-, diiodo-, and dinitro-*o*-cresoldiphenein, resorcinoldiphenein, tetrabromo-, and tetraiodoresorcinoldiphenein. While the corresponding derivatives of phenolphthalein dissolve in dilute sodium hydroxide solution to yield bright colored solutions, the substituted dipheneins yield yellowish solutions, indistinguishable from one another, in dilute alkali.

The absorption spectra of these compounds will be published subsequently.

Experimental

Tetrabromophenoldiphenein.—To 2 g. of a hot alcoholic solution of phenoldiphenein is added during one-half hour 4 g. of bromine and then one-half of the solvent is distilled off, a product separates which, purified from glacial acetic acid, gives a 75% yield of colorless crystalline tetrabromophenoldiphenein melting at 213–214°.

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[1] Professor Underwood died on March 20, 1934.

[2] Underwood and Kochmann, THIS JOURNAL, **45**, 3071 (1923); **46**, 2069 (1924).

[3] Underwood and Barker, *ibid.*, **52**, 4082 (1930).

Anal. Calcd. for $C_{26}H_{14}O_4Br_4$: Br, 45.07. Found: Br, 44.90, 44.45.

Diiodophenoldiphenein.—To 4 g. of phenoldiphenein in 60 cc. of 2 *N* potassium hydroxide are added with stirring during twenty minutes 10.8 g. of iodine and 11.2 g. of potassium iodide in 60 cc. of water and after twenty minutes the solution is made slightly acid with 6 *N* acetic acid. The reaction product is washed with 5% potassium iodide solution, dissolved in 5 *N* potassium hydroxide and reprecipitated with acetic acid. From the crude product, after boiling with 20 cc. of chloroform and recrystallizing from glacial acetic acid, a 20% yield of colorless diiodophenoldiphenein melting at 216–217° results.

Anal. Calcd. for $C_{26}H_{16}O_4I_2$: I, 39.29. Found: I, 39.31, 39.66.

Dinitrophenoldiphenein.—To 1 g. of phenoldiphenein suspended in 10 cc. of glacial acetic acid are added slowly with stirring and below 20° a mixture of 0.56 g. of nitric acid (sp. gr. 1.50) and 1.68 g. of sulfuric acid (sp. gr. 1.84). The reaction mixture is maintained at 45° for five minutes. Recrystallization of the precipitate from absolute alcohol gives yellow crystalline dinitrophenoldiphenein melting at 212.5–213°.

Anal. Calcd. for $C_{26}H_{16}O_8N_2$: N, 5.78. Found: N, 5.96, 5.89.

***o*-Cresoldiphenein.**—Ten grams of diphenic anhydride, 16 g. of *o*-cresol and 15 g. of fuming stannic chloride are heated at 125–135° for ten hours. The precipitate remaining after steam distillation is filtered, washed, extracted with 3 *N* potassium hydroxide and reprecipitated at 0° with 12 *N* hydrochloric acid. From the crude product, after washing with water and recrystallizing from glacial acetic acid, a 50% yield of colorless *o*-cresoldiphenein melting at 218.5–219.5° results.

Anal. Calcd. for $C_{28}H_{22}O_4$: C, 79.8; H, 5.24. Found: C, 79.0, 79.7; H, 5.35, 5.68.

Dibromo-*o*-cresoldiphenein.—To 2 g. of a hot alcoholic solution of *o*-cresoldiphenein are added slowly 5 g. of bromine and the solution refluxed twenty minutes; a product separates which, purified from absolute alcohol gives a 62% yield of colorless dibromo-*o*-cresoldiphenein melting at 203–204°.

Anal. Calcd. for $C_{28}H_{20}O_4Br_2$: Br, 27.54. Found: Br, 27.85, 27.65.

Diiodo-*o*-cresoldiphenein.—To 1 g. of *o*-cresoldiphenein in 15 cc. of 2 *N* potassium hydroxide are added slowly with stirring 2.7 g. of iodine and 2.8 g. of potassium iodide in 15 cc. of water, and after twenty minutes the solution is made slightly acid with 6 *N* acetic acid. The reaction product is dissolved in 10% potassium hydroxide and reprecipitated with 6 *N* hydrochloric acid. From the crude product, after washing with acetone and recrystallizing from absolute alcohol, a 43% yield of colorless diiodo-*o*-cresoldiphenein melting at 206–207° results.

Anal. Calcd. for $C_{28}H_{20}O_4I_2$: I, 37.69. Found: I, 37.80, 37.81.

Dinitro-*o*-cresoldiphenein.—To 1 g. of *o*-cresoldiphenein suspended in 10 cc. of glacial acetic acid are added slowly with stirring and below 20° a mixture of 0.57 g. of nitric acid (sp. gr. 1.50) and 1.70 g. of sulfuric acid (sp. gr. 1.84). The reaction mixture is maintained at 45° for five minutes. Recrystallization of the crude product from benzene and from absolute alcohol gives yellow crystalline dinitro-*o*-cresoldiphenein melting at 212.5–213°.

Anal. Calcd. for $C_{28}H_{20}O_8N_2$: N, 5.46. Found: N, 5.23, 5.40.

Resorcinoldiphenein, tetrabromo- and tetraiodoresorcinoldiphenein have been prepared previously.[2,4] Crystallization of resorcinoldiphenein from absolute alcohol gave a pale yellow product which melted at 248–249°. Tetrabromoresorcinoldiphenein was prepared as a brownish-yellow powder which melted at 271–272°. Tetraiodoresorcinoldiphenein was obtained as a greenish-yellow powder which melted at 208.5–209.5°.

Summary

1. The preparation of tetrabromo-, diiodo-, dinitrophenoldiphenein and *o*-cresoldiphenein, dibromo-, diiodo- and dinitro-*o*-cresoldiphenein has been described.

2. All of the known substitution products of phenoldiphenein dissolve in dilute sodium hydroxide with the development of a pale yellow color.

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(4) A. T. Wilson, Bachelor of Science Thesis, M. I. T., 1932.

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Absorption Spectra of Dipheneins

BY H. W. UNDERWOOD, JR., LOUIS HARRIS AND GEORGE BARKER

The fact that alkaline solutions of the dipheneins showed only a faint yellow color as compared with the deep colors observed in the phthaleins prompted a study of their absorption spectra. If the supposed quinoid structure of phenolphthalein (alkaline) is responsible for its color, there is the possibility that this characteristic structure is also present in the dipheneins, but the absorption band is displaced from the visible to the violet. On the other hand, there are the additional possibilities that the structure of the dipheneins is not analogous to that of the phthaleins or that the effect of the diphenic acid group is to minimize the effectiveness of the "quinoid" structure and so give only a weak absorption band in the visible.