heptene in 200 ml. of liquid ammonia was treated with 11.5 g. (0.5 mole) of sodium dissolved in 200 ml. of liquid ammonia. It was necessary to add 1 ml. more of the ester to effect complete decolorization of sodium. The mixture was hydrolyzed by careful addition of 250 ml. of water. The organic layer was washed twice with water, dried over calcium chloride, and distilled. Distillation was complete between 146–151° to give 23 g. (77% yield) of methyl amyl ketone. The semicarbazone melted at 122°.

Summary

Cleavage of alkenyl esters R—COO—C(R)=CH_2 with hydrogen bromide, hydrogen chloride, methanol, sodium in liquid ammonia and iodine in liquid ammonia is reported and the products described.

NOTRE DAME, INDIANA RECEIVED MARCH 9, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

Anthranol-beta-*d*-glucoside[1]

BY JOHN H. GARDNER[2] AND THOMAS F. MCDONNELL

In view of the suggestion of Hauser[3] that barbaloin is a *d*-arabinoside of aloe-emodin anthranol, since it yields aloe-emodin anthrone on hydrolysis with borax solution, we have prepared anthranol-β-*d*-glucoside as the most readily obtained analogous compound and have studied its hydrolysis under a variety of conditions by the methods used previously in the study of glycosides of various mono- and dihydroxyanthraquinones.[4] It was found that anthranol-β-*d*-glucoside is hydrolyzed completely by 0.05 *N* hydrochloric acid in one hour and by 0.05 *N* potassium hydroxide in thirty minutes. Hydrolysis was 62.4% complete in one hour with 9% borax. All hydrolyses were carried out at 100°. In the acid hydrolysis, pure anthrone was recovered, but with potassium hydroxide a part of the product was oxidized to dianthrone. The hydrolysis product formed with borax was not separated from unchanged glucoside and consequently was not identified.

These results differ markedly from the behavior of barbaloin in several ways. Notably, aloin is hydrolyzed extremely slowly by hydrochloric acid yielding chiefly a red, resinous material with a small amount of aloe-emodin, an anthraquinone derivative. No evidence of the formation of aloe-emodin anthrone under these conditions has ever been found. Reasoning by analogy, it seems extremely improbable that aloin could be an arabinoside of aloe-emodin anthranol.

(1) Anthracene Series. XII.

(2) This investigation was made possible by a grant to the senior author from a fund given to Washington University by the Rockefeller Foundation for research in science.

(3) Hauser, *Pharm. Acta Helv.*, **6**, 79 (1931).

(4) Gardner, McDonnell and Wiegand, THIS JOURNAL, **57**, 1074 (1935); Foster and Gardner, *ibid.*, **58**, 597 (1936); Gardner and Demaree, *ibid.*, **58**, 757 (1936).

Experimental

Anthranol-tetraacetyl-β-*d*-glucoside.—To a solution of 0.25 g. of potassium hydroxide in 50 cc. of acetone and 25 cc. of water there were added 0.8 g. of anthrone and 1.7 g. of acetobromoglucose. The flask was closed quickly with a stopper provided with a stopcock and evacuated until the solvent boiled. The evacuated flask was swirled vigorously until an orange solution had formed and it was then allowed to stand at room temperature for five hours with occasional shaking. During this time, the solution became lemon yellow and a magma of fine needles precipitated. The reaction mixture was then diluted to 150 cc. with water and filtered. The cream colored solid was stirred into 15 cc. of methyl alcohol and filtered, leaving 0.6 g. (28%) of nearly pure anthranol-tetraacetyl-β-*d*-glucoside. After recrystallizing four times from ethyl alcohol, it formed long colorless needles, m. p. 205–205.2°.

Anal. Calcd. for $C_{28}H_{28}O_{10}$: C, 64.1; H, 5.38. Found: C, 64.0, 64.4; H, 5.54, 5.33.

Anthranol-β-*d*-glucoside.—A suspension of 0.6 g. of anthranol-tetraacetyl-β-*d*-glucoside in 75 cc. of 50% ethyl alcohol was heated to 60° and treated with 1 g. of barium hydroxide in 20 cc. of water. The mixture was maintained at 60° for fifteen minutes, with mechanical stirring. It was then cooled in ice and made slightly acid with dilute sulfuric acid. The precipitated barium sulfate was filtered out and the filtrate was concentrated under reduced pressure to 20–25 cc. The cream colored solid which separated was filtered out, crystallized from 25% ethyl alcohol and dried over sulfuric acid in a vacuum; m. p. 204–206°. Mixed with an equal quantity of the tetraacetyl glucoside, it melted at 175–187°. Its solutions in alcohol and other common solvents showed a brilliant blue fluorescence.

Anal. Calcd. for $C_{20}H_{20}O_6 \cdot H_2O$: C, 64.1; H, 5.92. Found: C, 63.7; H, 5.33.

A sample was dried in a Pregl microdesiccator for thirty minutes at 110° in a current of dry air.

Anal. Calcd. for $C_{20}H_{20}O_6$: C, 67.4; H, 5.62. Found: C, 66.7; H, 5.41.

Hydrolysis Experiments.—As our supply of the glucoside was limited because of the poor yields, no attempt was

made to determine the extent of hydrolysis for varying periods of time. Instead, one experiment with each was carried out, using 0.05 *N* hydrochloric acid, 0.05 *N* potassium hydroxide and 9% borax at 100°. With hydrochloric acid, hydrolysis was complete in one hour and with potassium hydroxide, in thirty minutes. With borax, the glucoside was hydrolyzed 62.4% in one hour. The insoluble product of acid hydrolysis was quite pure anthrone (m. p. 154–155.5°), but with potassium hydroxide, some oxidation to dianthrone occurred. The insoluble product of borax hydrolysis was not obtained free from unchanged glucoside.

Summary

Anthranol-β-*d*-glucoside has been prepared and has been found to be hydrolyzed easily in acid and alkaline media.

ST. LOUIS, MISSOURI RECEIVED MARCH 6, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Chemistry of the Lipides of Tubercle Bacilli. XLVII. The Composition of the Avian Tubercle Bacillus Wax[1]

BY R. E. REEVES[2] AND R. J. ANDERSON

In paper X of this series Anderson and Roberts[3] described the extraction and fractionation of the lipides of the avian tubercle bacillus and it was found that the crude chloroform-soluble wax amounted to 70.7% of the total lipides and 10.79% of the dried bacterial mass. The present report deals with the properties and composition of the above mentioned wax. After the wax had been purified and saponified the cleavage products were found to consist of fatty acids, unsaponifiable matter and a water-soluble carbohydrate.

The fatty acids were a complex mixture of optically active hydroxy acids of very high molecular weight whose constitution we could not determine. None of the ordinary fatty acids could be found. The unsaponifiable matter consisted mainly of *d*-eicosanol-2 together with a small amount of *d*-octadecanol-2. The water-soluble carbohydrate was identified as trehalose.

The nature and kind of the cleavage products of the avian wax differentiate this material sharply from the previously examined wax of the human tubercle bacillus.[4] The latter product gave on saponification a mixture of fatty acids from which a hydroxy acid of high molecular weight, designated by the term "unsaponifiable wax," was isolated. The unsaponifiable matter contained the dihydric alcohol, phthiocerol, $C_{35}H_{72}O_3$,[5] while the water-soluble component was a specific polysaccharide which on hydrolysis yielded *d*-arabinose, galactose and other carbohydrates including inosite, mannose and glucosamine.

The avian wax shows considerable resemblance to the timothy bacillus wax which was recently analyzed by Pangborn and Anderson.[6] Both the avian and the timothy wax contain *d*-eicosanol-2, *d*-octadecanol-2 and trehalose together with new and previously unknown fatty acids of undetermined constitutions.

The object of the present investigation was not only to determine the chemical composition of the avian wax, which is quantitatively the most important fraction of the lipides of the avian tubercle bacillus, but also to provide sufficient quantities of the purified wax and of its cleavage products for physiological studies. The physiological experiments are being carried out by Dr. F. R. Sabin and collaborators of the Rockefeller Institute for Medical Research and will be reported independently.

Experimental Part

The crude wax isolated as described by Anderson and Roberts[3] was a non-crystalline powder of light yellow color. It was easily soluble in chloroform, ether, benzene, toluene, ligroin and ethyl acetate but it was insoluble in acetone, alcohol and methyl alcohol. The following constants were determined: m. p. 53–54°, iodine no. 7.8, saponification no. 77, $[\alpha]_D$ in $CHCl_3$ + 25.6°. A trace of phosphorus was present but sulfur, nitrogen and halogen were absent.

(1) An abstract of this paper was read before the Division of Organic Chemistry at the meeting of the American Chemical Society, Pittsburgh, Pa., September, 1936. The data are taken from the dissertation submitted by Richard E. Reeves to the Faculty of the Graduate School, Yale University, 1936, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. The present report is a part of a coöperative investigation on tuberculosis; it has been supported partly by funds provided by the Research Committee of the National Tuberculosis Association.

(2) Holder of a National Tuberculosis Association Graduate Student Fellowship at Yale University, 1934–1936.

(3) R. J. Anderson and E. G. Roberts, *J. Biol. Chem.*, **85**, 509 (1930).

(4) R. J. Anderson, *ibid.*, **83**, 505 (1929).

(5) F. H. Stodola and R. J. Anderson, *ibid.*, **114**, 467 (1936).

(6) M. C. Pangborn and R. J. Anderson, THIS JOURNAL, **58**, 10 (1936).