glucosamine is linked to streptose through carbon atom one of the amino sugar, and that streptobiosamine is linked to streptidine through the streptose moiety of the disaccharide.

The empirical formulas of the degradation products were consistently in best agreement with the formula $C_{21}H_{39}N_7O_{12}$ for streptomycin.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE COLLEGE]

Dehydration of Cholic Acid

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When cholic acid is dehydrated with anhydrous zinc chloride in acetic acid solution it yields an unsaturated compound by removal of the hydroxyl group from carbon number 7 and the hydrogen from number 8 carbon atom. The double bond rearranges to some other position, not yet fully agreed upon, yielding apocholic acid as the main product. Fieser[2] and Strain[3] have recently reviewed this work.

The object of this investigation was to study the effect of solvent and temperature upon the dehydration of cholic acid with zinc chloride. Of the number of solvents tried, acetone gave the best results.

Experimental

Dehydration in Acetone.—Fifty grams of anhydrous zinc chloride were dissolved in 225 g. of C. P. acetone; 50 g. of C. P. cholic acid[4] was added and the solution distilled over a steam-bath until it changed to a thin light orange-colored sirup. The flask was immediately weighed and, by difference in weight, found to contain 60 g. of acetone. Nine hundred and fifty ml. of cold water, acidified with three ml. of acetic acid, was added slowly while shaking with a whirling motion. The mixture was allowed to stand until the precipitate was crystalline; the water solution was decanted through a suction filter and the residue washed nearly free of chlorides. The precipitate was transferred back to the flask and the product dissolved in 100 ml. of boiling alcohol, then precipitated as before. After a third precipitation the product was dried in a non-oxidizing atmosphere.

The dry product was taken up in 300 ml. of hot absolute alcohol and filtered into a round bottom flask. The alcohol was evaporated over an oil-bath until the mixture had changed to a thin sirup. After a second alcohol treatment, 100 ml. of *m*-xylene was added rapidly while the solution was shaken with a whirling motion. After standing overnight, the crystalline mass was thoroughly broken up, filtered at the pump, and washed with xylene. The adhering xylene was removed by carefully heating to 134–140° in a non-oxidizing atmosphere. Thirty-five and five-tenths grams (75% yield) of the white product was obtained which was apparently nearly free of xylene. The yield of crystalline dehydrated product was decreased if heating was continued too long but when the heating period was too brief the product was found to contain unchanged cholic acid.

Properties of Product.—M. p.[5] 166–168°; mixed with product from acetic acid method (see below) the m. p. was unchanged; reacted rapidly with bromine and dilute alkali potassium permanganate showing unsaturation; neut. equiv. 396 (theoretical for apocholic acid, 390.5); X-ray diffraction photograph was the same as that from the acetic acid method.

Eight grams (17%) more of the crystalline product, melting at 154–159°, was obtained from the xylene filtrate by evaporating most of the xylene, adding absolute alcohol and crystallizing as above.

Dehydration in Acetic Acid.[6]—Five grams of anhydrous zinc chloride was dissolved in 150 ml. of glacial acetic acid, 50 g. of C. P. cholic acid added and the mixture refluxed forty minutes. It was then cooled and the product precipitated by adding, while shaking, 800 ml. of 2.5 *M* sodium hydroxide solution. After standing a few hours, the water solution was filtered off and the precipitate taken up in 600 ml. of 4% sodium hydroxide solution. The product was precipitated with hydrochloric acid, filtered off and washed free of chlorides. The remainder of the preparation was the same as the above procedure with acetone. The yield was 23.5 g. (48.6%). The properties of the slightly colored product were the same as those for the product from the acetone method.

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Summary

1. A simple method for dehydration of cholic acid with zinc chloride in acetone has been worked out which gives an excellent yield of dehydrated product.

2. From the melting point, unsaturation reactions, reaction-rate with iodine and bromide X-ray diffractions patterns the product seems to be the same as that obtained when cholic acid was dehydrated with zinc chloride in acetic acid solution. The acetone preparations, however, were whiter than those obtained by using the usual acetic acid method.

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(2) L. F. Fieser, "Chemistry of Natural Products Related to Phenanthrene," 2d ed., Monograph no. 70, Reinhold Publishing Company, New York, N. Y., 1937, pp. 123, 132 and 368.

(3) "Organic Chemistry, An Advanced Treatise," Henry Gilman, Editor-in-chief, Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 1416.

(4) The cholic acid was purchased from a reliable company and since the neutralization equivalent was 410, it was apparently nearly free of solvent (theoretical neut. equiv. 408.5).

(5) Melting point in this paper are uncorrected.

(6) A modified procedure of Boedecker, *Ber.*, **53**, 1852 (1920); *ibid.*, **54**, 2489 (1921).