

and the Hagersalkowski⁴ tests for cholesterol, obtaining positive tests. Further identification of the crystals as cholesterol was accomplished by the preparation of the benzoate⁵ and acetate⁶ derivatives.

The high cholesterol content of the shrimp oil led to feeding tests for antirachitic potency of the oil by the authors and F. P. Brooks,⁷ giving encouraging results. Since the extract of shrimp waste amounts to 2.25% of the waste, a production of 80,000 pounds of cholesterol could have been accomplished by the extraction of the waste of the 1927 crop of shrimp.

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A Simple Method for the Preparation of Glycine.—The preparation of glycine by the classical method,¹ employing the reaction between monochloroacetic acid and ammonia, has proved generally unsatisfactory because of the lengthy procedures involved in the isolation of a product free from ammonia and chloride and because of the low yield of pure glycine resulting. Robertson² found after a careful study of the course of the reaction between monochloroacetic acid and ammonia, that the yield of glycine could be greatly increased by the use of a large excess of ammonia and that there occurred a corresponding decrease in the amount of imino-diacetic acid and trimethylene-amine-tricarboxylic acid, the principal impurities resulting from side reactions. Based upon this observation, he proposed a method in which a 60 to 1 molecular ratio of ammonia to monochloroacetic acid was employed. This increased the actual concentration of glycine formed in solution to 86% of the theoretical. While a 50% final yield of pure glycine was obtained, the isolation of the product was accomplished after the laborious and expensive procedure of removing the ammonium chloride by the use of silver oxide.

Since, when a large excess of ammonia was used, the concentration of glycine formed was large in comparison with the amount of side reaction products, the possibility of *direct* precipitation of glycine seemed worthy of investigation. As was suggested by Robertson, 60 moles of

⁴ D. Holde and E. Mueller, "Saponifiable Hydrocarbons, Fats and Waxes," 1922, p. 519.

⁵ S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1904, Vol. I, p. 172.

⁶ R. J. Anderson, *J. Biol. Chem.*, 71, 707 (1926).

⁷ F. C. Vilbrandt, R. F. Abernethy and F. P. Brooks, "Preliminary Report on the Antirachitic Properties of Shrimp Oil," *THIS JOURNAL*, 52, 4940 (1930).

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¹ Kraut, *Ann.*, 266, 295 (1891).

² G. R. Robertson, *THIS JOURNAL*, 49, 2889 (1927).

ammonia and 1 mole of monochloroacetic acid were allowed to react. The excess ammonia was distilled off and the resulting aqueous solution was concentrated to a small volume. When 95% methyl alcohol was added to this solution, glycine promptly crystallized out and a 72–74% yield of an impure product resulted. By careful recrystallization a 60–64% yield of ammonia and chloride-free glycine was obtained. Our work does not indicate that the use of pyridine with methyl alcohol in the precipitation of glycine is necessary as was reported by Boutwell and Kuick.³ As a result of our experiments, a simple, rapid and inexpensive method for the preparation of pure glycine is offered.

Experimental

Method of Preparation.—One mole (94.5 g.) of monochloroacetic acid is added gradually with shaking to 4 liters of ammonium hydroxide (sp. gr. 0.90) in a 5-liter round-bottomed flask. When all of the monochloroacetic acid is dissolved and the solution is thoroughly mixed, the flask is stoppered and set aside undisturbed for forty-eight hours at room temperature. The solution, which is colorless or faintly yellow, is then concentrated on a water-bath under reduced pressure to a volume of about 200 cc. The concentrated aqueous solution is then made up to 250 cc. with water and transferred to a 2-liter beaker, and the glycine is crystallized out by gradually adding, with stirring, 1500 cc. (six volumes) of 95% methyl alcohol (the use of absolute methyl alcohol offers no advantage). The mixture is placed in an ice box for four to six hours to allow complete crystallization. The supernatant liquid is then decanted from the crystals onto a Büchner funnel, the remaining crystals are suspended in approximately 500 cc. of 95% methyl alcohol, and are transferred to the filter. The beaker is rinsed twice with 100–120 cc. portions of 95% methyl alcohol, and the rinsings are poured over the crystals in the funnel. Finally, as much of the liquid as possible is pressed out, the crystals are washed with a small amount of ethyl ether, and dried in air. A yield of 54–55 g. of glycine, 72–74% of the theoretical, is obtained.

Since the product contains a trace of ammonia (by Nessler's reagent) and chloride (by silver nitrate), a second crystallization is carefully made by dissolving the crystals in 210–215 cc. of water, with warming, and precipitating with 5 volumes (1250 cc.) of 95% methyl alcohol. After crystallization in an ice box, the glycine is filtered, washed and dried, as previously outlined. A yield of 48–49 g., 64–65% of the theoretical, results. If the product still shows a faint trace of ammonia, a second recrystallization may be made, which will yield 45–48 g. The final product is white and finely crystalline. The recovery of further amounts of glycine from filtrates is not practicable because only a small amount

³ P. W. Boutwell and L. F. Kuick, *THIS JOURNAL*, **52**, 4166 (1930).

