XII was acetylated under conditions similar to those recorded by de Arce, Greene and Capps[6] for the acetylation of 5-amino-8-bromo-6-methylquinoline; yield 67%, m.p. >330° (uncor.) from 95% ethanol.

Anal. Calcd. for $C_{12}H_{12}N_2O_2$: N, 12.96. Found: N, 13.11.

XII was benzoylated under conditions similar to those used by de Arce, Greene and Capps[6] for the benzoylation of 5-amino-8-bromo-6-methylquinoline; yield 42%, m.p. > 315°.

Anal. Calcd. for $C_{17}H_{14}N_2O_2$: N, 10.07. Found: N, 10.00.

8-Methyl-5-quinolinearsonic Acid (XV), 2-Chloro-8-methyl-5-quinolinearsonic Acid (XVIII) and 2-Hydroxy-8-methyl-5-quinolinearsonic Acid (XXI).—The hydrochlorides of X (12.0 g.), XI (9.0 g.) and XII (10.0 g.) were diazotized and converted into arsonic acids according to the procedure reported by Capps and Hamilton[11] for changing certain 2-chloroaminoquinolines into 2-chloroquinolinearsonic acids. XV, XVIII and XXI resulted in yields of 12.8, 11.9 and 14.8%, respectively. XV melted at 224–226° while XVIII and XXI melted above 315° (uncor.).

Anal. Calcd. for $C_{10}H_{10}AsNO_3$: As, 28.05; N, 5.27. Found: As, 27.92; N, 5.09. Calcd. for $C_{10}H_9AsClNO_3$: As, 24.84; N, 4.65. Found: As, 24.69; N, 4.75. Calcd. for $C_{10}H_{10}AsNO_4 \cdot H_2O$: As, 24.87; N, 4.65. Found: As, 24.79; N, 4.67.

(11) J. D. Capps and C. S. Hamilton, THIS JOURNAL, **60**, 2105 (1938).

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Seroflocculating Steroids. I. Ethyl 3β-Chloro-Δ¹¹-cholenate[1]

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RECEIVED APRIL 2, 1954

During the course of our study of the relationship of steroids[2] to immunological phenomena associated with injury, we have had the occasion to investigate the seroflocculating reagents described by Penn and his associates.[3] These reagents[4] cause flocculation in a high percentage of the sera of patients with cancer and other diseases.

Our investigation of the flocculating reaction led us to prepare ethyl 3β-chloro-Δ¹¹-cholenate (I) which in preliminary testing we have found to be a very satisfactory flocculating reagent. The compound is crystalline and stable under ordinary conditions. We will discuss in detail elsewhere implications of general significance in this field suggested to us by this finding.

Treatment of ethyl 3α-hydroxy-Δ¹¹-cholenate (II) with phosphorus pentachloride in chloroform at 0° yielded ethyl 3β-chloro-Δ¹¹-cholenate (I), which could be quantitatively hydrogenated to ethyl 3β-chlorocholanate (III). The latter was found to be identical by melting point comparison with the product of reaction between ethyl lithocholate and phosphorus pentachloride.

(1) Aided in part by a grant from the United States Public Health Service.

(2) D. H. Sprunt, A. D. Dulaney and R. P. Conger, *Cancer Research*, **2**, 282 (1951).

(3) H. S. Penn, *J. Natl. Cancer Inst.*, **12**, 1389 (1952); A. H. Dowdy, H. S. Penn, G. Hall and A. Bellamy, *Proc. Am. Assoc. for Cancer Research*, **1**, 12 (1954).

(4) We wish to thank Drs. Dowdy and Penn and their group for their coöperation in making available to us procedures for preparing and testing both the liver and desoxycholic acid-derived flocculating reagents which they designate as "antigens."

Testing data on I and current studies on related compounds with flocculating activity will be reported in forthcoming publications.

Experimental[5,6]

Ethyl 3α-Hydroxy-Δ¹¹-cholenate (II).—3α-Hydroxy-Δ¹¹-cholenic acid[7,8] was esterified with absolute ethanol essentially according to the method used by Kendall and his associates for the preparation of the methyl ester.[9] However, whereas esterification with methanol is complete in less than an hour, with ethanol 27% of unreacted acid was recovered even after 22 hours. The ethyl ester did not crystallize from aqueous ethanol, but separated satisfactorily from purified Skellysolve F as colorless needles melting at 81–82°, $[\alpha]^{26}D$ + 30° (*c* 2.01, chf.). *Anal.* Calcd. for $C_{26}H_{42}O_3$: C, 77.56; H, 10.52. Found: C, 77.3; H, 10.6.

Ethyl 3β-Chloro-Δ¹¹-cholenate (I).[10]—To a stirred solution of 500 mg. of II in 28 ml. of chloroform, in a flask equipped with a drying tube and immersed in an ice-bath maintained at 0°, 800 mg. of powdered calcium carbonate and, in two portions with a 20-minute interval, 1.2 g. of phosphorus pentachloride were added. Stirring was continued for 100 minutes at 0°. The reaction product was poured into 200 ml. of 5% sodium bicarbonate solution containing ice, and ether was added. The resulting mixture was stirred until the ice had melted, transferred to a separatory funnel and shaken thoroughly. The organic layer, which still retained a small amount of an insoluble, colorless, inorganic solid, was washed with water, dried (Drierite), filtered and evaporated (reduced pressure) to a colorless residual oil. This oil dissolved in the minimum amount of warm methanol, on refrigeration for 2 hours yielded 380 mg. (73%) of colorless crystals m.p. 69–73°. Two recrystallizations from methanol gave thin plates melting at 74–76°, $[\alpha]^{26}D$ + 25° (*c* 2.05, chf.). *Anal.* Calcd. for $C_{26}H_{41}O_2Cl$: C, 74.16; H, 9.82; Cl, 8.42. Found: C, 74.3; H, 9.8; Cl, 8.8.

Catalytic Hydrogenation.—I in acetic acid solution and the presence of Adams catalyst absorbed 1.03 moles of hydrogen within 20 minutes. After removal of catalyst and solvent, two crystallizations of the product from methanol gave colorless, feathery crystals, m.p. 59–60.5°, which did not depress the melting point of ethyl 3β-chlorocholanate (III) prepared from ethyl lithocholate[11,12] by the same method as used for the unsaturated derivative, crystallizing in methanol as colorless needles, m.p. 59–61.5°, $[\alpha]^{26}D$ +18.5° (*c* 1.27, chf.). *Anal.* Calcd. for $C_{26}H_{43}O_2Cl$: C, 73.81; H, 10.24; Cl, 8.38. Found: C, 73.5; H, 10.5; Cl, 8.2.

(5) Microanalyses by the Microchemical Laboratory of New York University.

(6) Melting points were taken on an electrically heated micro hot-stage and are uncorrected.

(7) J. Press and T. Reichstein, *Helv. Chim. Acta*, **25**, 878 (1942); B. F. McKenzie, W. F. McGuckin and E. C. Kendall, *J. Biol. Chem.*, **162**, 555 (1946).

(8) Generously supplied by Merck and Co. through the kindness of Dr. Max Tishler.

(9) L. L. Engle, V. R. Mattox, B. F. McKenzie, W. F. McGuckin and E. C. Kendall, *J. Biol. Chem.*, **162**, 565 (1946).

(10) Although a double bond shift is considered unlikely under the conditions of this reaction, experiments are under way to confirm the position of unsaturation.

(11) F. Reindel and K. Niederländer, *Ber.*, **68**, 1969 (1935).

(12) We are indebted to Ciba Pharmaceutical Products, Inc., and Dr. H. B. MacPhillamy for a supply of lithocholic acid.

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The Preparation of Sarcosine and Methyl α-Methylamino-β-(3-indolyl)-propionate

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RECEIVED FEBRUARY 15, 1954

The preparation of methyl α-methylamino-β-(3-indolyl)-propionate was undertaken since a supply of this ester was required as an intermediate.