

(ps). The sample from authentic exaltone melted at 106–109° (ps), and there was no depression below 106° when both specimens were mixed. The *l*-menthydrazone<sup>24</sup> formed needles from dilute ethanol, m. p. 138.5–139.5°, and when mixed with an authentic specimen had the same melting point. *Anal.* Calcd. for C<sub>28</sub>H<sub>48</sub>O<sub>2</sub>N<sub>2</sub>: N, 6.7. Found: N, 6.7.

**Dehydration of Carbinol "A."**—Five grams of carbinol was heated with 15 g. of powdered fused potassium acid sulfate for two hours at 190–200°, then one hour more at 210°. The products were worked up as usual, and distilled, b. p. 116–121° (0.7 mm.), mostly 118.5–119°. It was redistilled from sodium, b. p. 128.5–129° (1 mm.), 3.2 g. The distillate partially solidified when chilled. After laborious fractional crystallization from methanol, the needles melted at 45.9–46.9°. *Anal.* Calcd. for C<sub>17</sub>H<sub>32</sub>: C, 86.4; H, 13.6. Found: C, 86.4; H, 13.8.

**Reduction of Cycloheptadecene.**—The above hydrocarbon, 0.45 g., absorbed one equivalent of hydrogen rapidly in ether-acetic acid solution with Adams platinum catalyst (calcd., 66 cc. hydrogen; found, 68 cc.).<sup>25</sup> The product was freed of acid by extraction with caustic, the ethereal solution was evaporated, and the residue was recrystallized from methanol, yielding long slender needles, m. p. 66.0–66.2°, *n*<sub>D</sub><sup>20</sup> 1.4538. *Anal.* Calcd. for C<sub>17</sub>H<sub>34</sub>: C, 85.6; H, 14.4. Found: C, 85.3; H, 14.5.

(24) Prepared according to Woodward, Kohman and Harris, *THIS JOURNAL*, **68**, 120 (1941). We are indebted to Dr. R. B. Woodward for the *l*-menthydrazone used.

(25) We are indebted to Dr. R. C. Jones for assistance in this reduction.

**Reduction of Civetone.**—Authentic civetone (0.35 g.; Firmenich and Co., New York) was hydrogenated as above, but in pure ether solution.<sup>25</sup> The correct amount of hydrogen for one double bond was absorbed rapidly, the carbonyl group remaining completely unattacked. The ether was evaporated, and the residue converted directly to the semicarbazone, which, after two recrystallizations from methanol, melted at 190–190.5° (ps). When mixed with the semicarbazone of ketone "A," no depression was observed. Regeneration with oxalic acid yielded the pure ketone, m. p. 64–65° (ps). A mixture with ketone "A," m. p. 59–61° (ps), melted at 60.5–62° (ps).

## CRYSCOPIC DATA

C <sub>17</sub> H <sub>32</sub> , mg.	Naphtha- lene, mg.	M. p. pure, °C.	M. p. mixt., °C.	<i>t.</i> , °C.	Con- stant
25.762	1.093	46.5	39.7	6.8	20.5
30.173	1.983	46.5	36.3	10.2	19.9
Average					20.2

## Summary

1. The scent glands of the Louisiana muskrat contain a mixture of cyclopentadecanol and cycloheptadecanol, and the corresponding ketones.
2. The cryoscopic constant of cycloheptadecene has been determined.

CAMBRIDGE, MASSACHUSETTS

BATON ROUGE, LOUISIANA RECEIVED SEPTEMBER 20, 1941

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

## Sterols. CXXV. Sapogenins. LI. The Structure of the Dibasic Acid Obtained by the Permanganate Oxidation of Anhydrosarsasapogenic Acid

BY RUSSELL E. MARKER AND ANTHONY C. SHABICA

Our experimental work shows that the dibasic acid obtained on the oxidation of anhydrosarsasapogenic acid by potassium permanganate cannot have the structure (III) given by Fieser and Jacobsen.<sup>1</sup> We suggest structure II for this acid.

We wish to thank Parke, Davis and Company for their assistance.

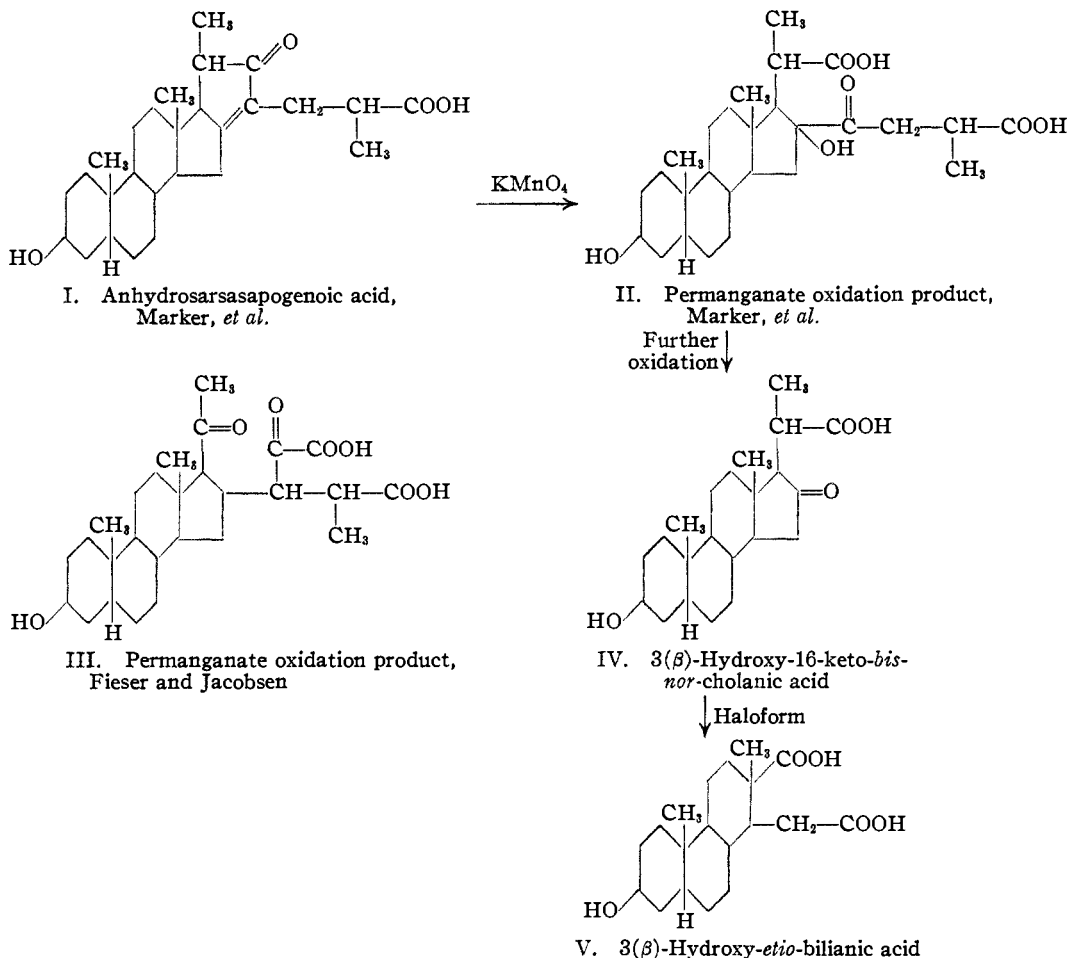
**Alkaline Permanganate Oxidation of Anhydrosarsasapogenic Acid.**—To 2.1 g. of pure anhydrosarsasapogenic acid (m. p. 241–243° dec.) suspended in 80 cc. of water was added 20 cc. of 2% sodium hydroxide solution. The mixture was cooled to –5° and an excess of 2% potassium permanganate added dropwise with stirring. The solution was then allowed to remain at room temperature for thirty minutes with an excess of potassium permanganate solution. It was slowly filtered through kieselguhr at room temperature, acidified with dilute sulfuric acid and the precipitated solid was extracted with ether. The ethereal

solution was washed with water and evaporated to a volume of 100 cc. After standing, the fine white crystals were filtered and recrystallized from ether as white prisms, m. p. 285–287° dec. This gave no depression when mixed with an authentic sample of 3(β)-hydroxy-16-keto-*bis-nor*-cholic acid. A yield of 650 mg. of pure product was obtained.

*Anal.* Calcd. for C<sub>22</sub>H<sub>34</sub>O<sub>4</sub>: C, 72.9; H, 9.5. Found: C, 72.6; H, 9.4.

**Alkaline Permanganate Oxidation of the Dibasic Acid Obtained from the Cold Permanganate Oxidation of Anhydrosarsasapogenic Acid.**—To 250 mg. of pure dibasic acid (m. p. 206–207° dec.) suspended in 20 cc. of water was added 7 cc. of 2% sodium hydroxide solution. To the mixture an excess of 2% potassium permanganate solution was added dropwise, with stirring, at room temperature. It was allowed to stand for thirty minutes. The solution was filtered, acidified with dilute sulfuric acid and extracted with ether. The ethereal solution was washed with water and evaporated, yielding a product which was not purified.

(1) Fieser and Jacobsen, *THIS JOURNAL*, **60**, 2753 (1938).



The residue was dissolved in 250 cc. of absolute ethanol, and to the boiling solution was added 12.0 g. of sodium over a period of ninety minutes. The resulting solution was cooled, diluted with water, acidified with dilute sulfuric acid and the precipitated white solid was extracted with ether. The ethereal extract was washed with water, 3% sodium hydroxide solution and finally with water and evaporated. The crystalline residue was crystallized from ether-pentane in small white needles, m. p. 200–202°. This gave no depression in melting point when mixed with sarsasapogenin lactone. A yield of 140 mg. of pure product was obtained.

*Anal.* Calcd. for  $C_{22}H_{34}O_3$ : C, 76.25; H, 9.9. Found: C, 76.0; H, 9.8.

When refluxed with acetic anhydride an acetate was obtained which crystallized from ether-pentane in white needles, m. p. 182–184°. This gave no depression in melting point when mixed with an authentic sample of the acetate of sarsasapogenin lactone.

**Chromic Anhydride Oxidation of the Ester Acetate of the Dibasic Acid Obtained by the Cold Permanganate Oxidation of Anhydrosarsasapogenoic Acid.**—To 1.0 g. of the pure dibasic acid prepared by the method of Fieser and Jacobsen<sup>1</sup> dissolved in 150 cc. of ether was added a cold ethereal solution of diazomethane. The solution was allowed to stand at room temperature until the evolution of

nitrogen ceased. The ether was distilled and the residue was refluxed for thirty minutes with 25 cc. of acetic anhydride. The excess acetic anhydride was evaporated *in vacuo* and the residue was dissolved in 100 cc. of glacial acetic acid. To this solution was added 1.0 g. of chromic anhydride in 20 cc. of 80% acetic acid. The mixture was heated at 60° for three hours, cooled, diluted with water and extracted with ether. The ethereal extract was washed with water and evaporated. The residue was reduced with sodium and absolute methanol, according to the previous directions, and the lactone fraction crystallized from ether-pentane, m. p. 200–202°. This gave no depression in melting point when mixed with an authentic sample of sarsasapogenin lactone.

*Anal.* Calcd. for  $C_{22}H_{34}O_3$ : C, 76.25; H, 9.9. Found: C, 75.8; H, 9.9.

**Haloform Reaction of 3(β)-Hydroxy-16-keto-bis-nor-cholanic Acid.**—A solution of 400 mg. of pure 3(β)-hydroxy-16-keto-bis-nor-cholanic acid (m. p. 285–287° dec.) and 6 cc. of 10% sodium hydroxide solution was treated with a potassium iodide-iodine solution until the color persisted for two minutes at 60°. Upon dilution with water a yellow precipitate of iodoform separated which was filtered. The solution was acidified with dilute sulfuric acid and the precipitated solid was extracted with ether. The ethereal extract was washed with water,

sodium bisulfite and finally with water. The residue from evaporation of the solvent was crystallized from chloroform in plates, m. p. 216–218°. A mixed melting point with an authentic sample of 3-hydroxy-*etio*-bilianic acid gave no depression. A yield of 110 mg. of pure product was obtained.

*Anal.* Calcd. for  $C_{19}H_{30}O_5$ : C, 67.4; H, 8.9. Found: C, 67.1; H, 9.0.

When refluxed with acetic anhydride and sublimed in high vacuum, the sublimate gave a product which was crystallized from ether-pentane in small prisms, m. p. 198–201°. This gave no depression in melting point when

mixed with an authentic sample of the acetate anhydride of 3( $\beta$ )-hydroxy-*etio*-bilianic acid.

*Anal.* Calcd. for  $C_{21}H_{30}O_5$ : C, 69.6; H, 8.3. Found: C, 69.7; H, 8.4.

### Summary

The structure assigned by Fieser and Jacobsen<sup>1</sup> to the potassium permanganate oxidation product of anhydrosarsasapogenoic acid is shown to be wrong. We suggest a new structure of this acid.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

## The Use of Bunte Salts in Synthesis. III. The Preparation of Aliphatic Disulfides<sup>1</sup>

BY HARRY E. WESTLAKE, JR.,<sup>2</sup> AND GREGG DOUGHERTY

Sodium alkylthiosulfates, or Bunte salts, have been reported to form disulfides readily by pyrolysis,<sup>3</sup> electrolysis,<sup>4</sup> reaction with iodine,<sup>5</sup> and reaction with hydrogen peroxide.<sup>6</sup> Of these methods, the last two appeared to give the most satisfactory results. However, their discoverers prepared only a few disulfides, none of which were normal alkyl compounds. We have undertaken, therefore, the preparation of representative members of this latter type, and have obtained varying, but, on the whole, good yields. To the compounds previously prepared by the iodine reaction, namely, benzyl and *o*-nitrobenzyl disulfides and dimethyl dithioglycolate, we have added butyl, heptyl, octyl, dodecyl, and octadecyl disulfides. Twiss had prepared benzyl, *o*-nitrobenzyl, *p*-nitrobenzyl, and allyl disulfides by the peroxide reaction. To these we have added butyl, heptyl, octyl and dodecyl disulfides. The method appears to be an excellent one for any radical whose Bunte salt can be easily formed.

The intermediate stages of these reactions appear to be highly complicated. As Price and Twiss pointed out,<sup>4</sup> the mechanism probably does not consist of hydrolysis to the mercaptan and the subsequent oxidation of that compound. We have made a study of the process and hope to publish the results in a later paper.

(1) Previous papers: Westlake and Dougherty, *THIS JOURNAL*, **63**, 658 (1941); Stoner and Dougherty, *ibid.*, **63**, 987 (1941).

(2) Now at the Mellon Institute of Industrial Research, Pittsburgh, Pa.

(3) Bunte, *Ber.*, **7**, 646 (1874).

(4) Price and Twiss, *J. Chem. Soc.*, **91**, 2021 (1907); **93**, 1395, 1401 (1908).

(5) Price and Twiss, *ibid.*, **95**, 1489 (1909).

(6) Twiss, *ibid.*, **105**, 36 (1914).

### Experimental

The procedure used was that of Price and Twiss with some modifications due to the liquid nature of certain of the products. The Bunte salt solution was prepared in the usual manner<sup>7</sup> and then either iodine was added in small portions until the color remained, or cooled and allowed to stand with peroxide. The liquid products were extracted with ether; the extract was then evaporated and the residual oil distilled under a vacuum. When the product was solid, it was crystallized from alcohol or acetic acid. If economy is desired, the iodine can be recovered by passing chlorine through the aqueous layer after separation of the product.<sup>8</sup>

*n*-Butyl Disulfide.—Thirty-eight and one-tenth grams (0.3 mole) of *n*-butyl bromide and 74.4 g. (0.3 mole) of sodium thiosulfate were dissolved in a mixture of 225 cc. of alcohol and 225 cc. of water. The mixture was refluxed until the solution was homogeneous. Then iodine crystals were added in small portions until the color remained. The mixture was transferred to a separatory funnel and the water layer drawn off and extracted with ether. The extract was evaporated and the residual oil was combined with the rest of the product. This was washed with aqueous sodium bisulfite to remove iodine and then dried with sodium sulfate. It boiled at 90–100° (3 mm.),<sup>9</sup> yield 57%.

When the hydrogen peroxide reaction was used, the Bunte salt solution was cooled and allowed to stand at 5° with 40 cc. of 30% hydrogen peroxide and a few drops of dilute sulfuric acid as a catalyst. After several days the product was isolated as before, yield 56%.

*n*-Heptyl Disulfide.—This compound was prepared by the same procedure used for butyl disulfide; yield, by the iodine reaction, 66%; by the peroxide reaction, 65%; boiling point 143–147° (5 mm.). Since this compound could not be found in the literature, it was analyzed. Calcd. for  $C_{14}H_{28}S_2$ : S, 24.81. Found: S, 24.87.

(7) See the first paper of this series, Westlake and Dougherty, *THIS JOURNAL*, **63**, 658 (1941).

(8) See Mellor, "Treatise on Inorganic Chemistry," Vol. II, p. 41.

(9) Hunter and Sorenson, *THIS JOURNAL*, **54**, 3364 (1932).