

Four almost equal fractions were obtained: 80–100°, 100–120°, 120–200°, and a non-distillable residue. The sublimate distilling at 120–200° was in the range in which one would expect to find the pregnanediols if present. As these are quite insoluble in acetone, each of the four fractions was dissolved in an equal volume of this solvent, but no product crystallized. The fraction also resisted crystallization from other solvents. Therefore, the total sublimate was combined and refluxed for ten hours with an equal weight of sodium in 100 cc. of dry xylene. If *allo*-pregnanediol had been present it would have been converted to the configuration at the 3-hydroxyl which would precipitate with digitonin. But when the isomerized product was treated with alcoholic digitonin, less than 100 mg. of insoluble digitonide was formed, showing the absence of *allo*-pregnanediol. This fraction was then oxidized with chromic acid in acetic acid at room temperature for thirty minutes. Only 4 g. of ketonic materials was obtained from 24 g. of carbinol, the remainder being acids. Upon sublimation of the ketones no crystalline product could be obtained.

The non-distillable carbinol fraction (9 g.) was oxidized by dissolving in 150 cc. of acetic acid and adding 4 g. of chromic anhydride in 25 cc. of 80% acetic acid. After

standing for thirty minutes, water was added. The product, isolated in the usual manner, was treated with Girard's reagent and the ketonic fraction (1.3 g.) sublimed in a high vacuum. The fraction distilling at 100–120° crystallized from dilute methanol, giving androstanedione, m. p. 125–128°, which gave no depression in melting point when mixed with an authentic sample.

*Anal.* Calcd. for  $C_{19}H_{28}O_2$ : C, 79.1; H, 9.8. Found: C, 79.0; H, 9.9.

### Summary

The steroidal content of steers' urine was investigated. Unlike bulls' urine, steers' urine contains no pregnanediols. A relatively large amount of cholesterol but no equistanol was found. The ketonic fraction gave androsterone, dehydroisoandrosterone and estrone in approximately the same proportions as found in bulls' urine. The non-distillable carbinols gave a small amount of androstanedione on oxidation. The characteristic urinary hydrocarbon,  $C_{28}H_{58}$ , was found.

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## NOTES

### Esterification of Highly Hindered Acids

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Esterification of highly hindered acids is generally very difficult to accomplish by direct methods. Satisfactory yields of methyl esters have been obtained, however, by thermal decomposition of the corresponding tetramethylammonium salts according to the procedure of Prelog and Piantanida.<sup>1</sup> The method is based on observations of Lawson and Collie<sup>2</sup> and involves a reaction which is closely related to that which occurs when betaines are decomposed thermally.<sup>3</sup>

The method has now been applied to 2,4,6-trimethyl- and 2,4,6-triethylbenzoic acids to determine the influence of excessive hindrance. Tetramethylammonium hydroxide made by the method of Walker and Johnson<sup>4</sup> was employed to make the tetramethylammonium salts. These

(1) Prelog and Piantanida, *Z. physiol. Chem.*, **244**, 56 (1936).

(2) Lawson and Collie, *J. Chem. Soc.*, **53**, 631 (1888).

(3) Willstätter, *Ber.*, **35**, 587 (1902); Willstätter and Kahn, *ibid.*, **37**, 401, 1853 (1904); Prelog, *Coll. trav. chim. Tchech.*, **2**, 712 (1930); Kuhn and Giral, *Ber.*, **68**, 387 (1935).

(4) Walker and Johnson, *J. Chem. Soc.*, **87**, 955 (1905).

were decomposed by heating to 200–250°. The yields of pure methyl esters varied from 63 to 90% of the theoretical amounts.

The methyl 2,4,6-triethylbenzoate is a new compound. It boils at 114–115° (5 mm.);  $n_D^{20}$  1.5012;  $d_4^{20}$  0.982.

*Anal.* Calcd. for  $C_{14}H_{20}O_2$ : C, 76.86; H, 9.47. Found: C, 76.59; H, 9.48.

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### The Isolation of a Crystalline Substance from Starches Oxidized by Periodate

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By degrading various periodate oxy-starches with acid methyl alcohol,<sup>1</sup> we have isolated a white, crystalline, levorotatory compound with the formula  $C_{13}H_{16}O_8(OCH_3)_4$  and m. p. 150–150.5° (corr.). Although stable to further oxidation with periodate or Fehling's solution, the substance

(1) Jackson and Hudson, *THIS JOURNAL*, **60**, 989 (1938).