

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.

STATE COLLEGE, PENNA. RECEIVED FEBRUARY 27, 1939

NOTES

Esterification of Highly Hindered Acids

BY REYNOLD C. FUSON, JOSEPH CORSE AND E. C. HORNING

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.¹ The method is based on observations of Lawson and Collie² and involves a reaction which is closely related to that which occurs when betaines are decomposed thermally.³

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 Johnson⁴ 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

BY D. H. GRANGAARD, J. H. MICHELL AND C. B. PURVES

By degrading various periodate oxy-starches with acid methyl alcohol,¹ 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).

readily reduced the latter after mild acid hydrolysis and appeared to be the methyl acetal of an aldehyde or ketone. This in turn was possibly a fragment of a still larger chemical unit which was oxidized with the starch. No conclusive evidence was obtained to indicate whether the crystals were derived from an integral part of the starch macromolecule or from an associated impurity.

The crystalline material was obtained in 0.7 to 0.9% yield from high grade commercial specimens of corn, wheat, potato and arrowroot starches. It was also isolated from soluble potato starch² which after being oxidized was dialyzed against water for four days. Preliminary experiments with xylan gave none of the substance while with cellulose the trace of apparently crystalline material observed was too minute to be identified with certainty.

This note is published because only two of us (J. H. M. and C. B. P.) intend to continue the investigation.

Experimental

Sodium periodate, 34.0 g. or 0.116 mole of $\text{Na}_3\text{H}_2\text{IO}_6$ was shaken at room temperature with 500 cc. of water and 50 cc. of glacial acetic acid until as much as possible had been dissolved. Starch, 20.25 g. air dry or 0.114 mole dry, was then added and the mixture, pH about 4.2, gently agitated until the next day, when titration³ showed that all of the periodate had reacted. The oxy-starch was filtered off, washed free of iodate, completely dried in a desiccator and suspended in dry methanol containing 10% of hydrogen chloride. Five hours of heating under a reflux condenser completed the degradation and after the removal of acid as the lead salt the solvent was evaporated. The viscid, levorotatory residue was dissolved in 70 cc. of 0.2 *N* aqueous caustic soda, the solution was almost saturated with sodium chloride and extracted with a total volume of 1500 cc. of diethyl ether. After drying, the extract yielded a pale yellow oil which partly crystallized when alternately cooled in dry-ice and allowed to thaw. The same crystals also separated from the high-boiling fraction of the oil (b. p. 170–180° at 3–4 mm.). Two recrystallizations from ether left the m. p. constant at 150–150.5° (corr.) and not depressed by admixture with specimens derived from other starches. The yield of pure material was 0.15 to 0.17 g. for the different starches and either sodium or potassium periodate, buffered to pH 4.2 with acetate or phthalate, was used in the preparation.

Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_8(\text{OCH}_3)_4$: C, 48.11; H, 6.60; OCH_3 , 29.24; mol. wt., 424. Found for two independent preparations: C, 48.21, 47.77, 47.75; H, 6.61, 6.59, 6.63; OCH_3 , 28.87, 29.09, 29.20; mol. wt. (Rast), 419, 425, 428, 432 for 3–10% solutions.

The substance was sparingly soluble in water and petroleum ether but dissolved more readily in other solvents.

(2) Baird, Haworth and Hirst, *J. Chem. Soc.*, 1201 (1935).

(3) Treadwell and Hall, "Analytical Chemistry," 8th ed., Vol. II, John Wiley and Sons, Inc., New York, p. 616.

The specific rotation at 26° in dioxane was -7.1° (sodium light, *C*, 0.911).

CONTRIBUTION No. 188

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The Dissociation Constant of Hypobromous Acid

BY MANFRED KIESE AND A. BAIRD HASTINGS

In experiments on the catalytic effect of certain acids upon the hydration of carbon dioxide, it became necessary to know the dissociation constant of hypobromous acid. No data on this constant were found in the literature.

Hypobromous acid was prepared by allowing bromine in aqueous solution to react with mercuric oxide. The acid was purified by distillation in vacuum. Since hypobromous acid is not very stable, the experiments were carried out immediately after the preparation of the acid, in a constant temperature room, at a solution temperature of 5°.

The dissociation constant was estimated from data obtained by the titration of 0.07 *M* solutions of hypobromous acid with 0.7 *N* sodium hydroxide; pH was measured potentiometrically, using the glass electrode and a saturated calomel cell. The standard of reference used in the calculation of the pH values was "standard" acetate assuming its pH = 4.65.¹ Three titration curves were determined (obtaining from 15 to 20 points for each curve), and the dissociation constants calculated by application of the mass law equation. The average value of the apparent dissociation constant was found to be 1.0×10^{-9} , or expressed logarithmically $pK' = 9.0 \pm 0.06$.

It may be noted that the value of pK found for hypobromous acid lies between that reported for hypochlorous acid, $pK = 7.6$,² and that for hypiodous acid, $pK = 10.6$.³

(1) D. I. Hitchcock and A. C. Taylor, *THIS JOURNAL*, **59**, 1812 (1937).

(2) References in Gmelin, *Handbuch der anorg. Chemie*, Vol. VI, 1927, p. 255.

(3) F. Fürth, *Z. Elektrochem.*, **26**, 57 (1922).

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Sterols. LXII. Position of the Hydroxyl Group in Tigogenin and Sarsasapogenin

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Until the present time no substantial chemical evidence has been given which would distinguish