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 starch[2] 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 $Na_3H_2IO_6$ 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 titration[3] 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 $C_{13}H_{16}O_8(OCH_3)_4$: 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).

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 hypoiodous 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.*, **28**, 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