

Neither dibenzyl sulfoxide or benzmorpholide were reducible under the conditions used, but benzthiomorpholide was reducible with the results listed in Table I. Concentration studies in acetate buffer of pH 4.0, phosphate buffer of pH 8, and borate buffer of pH 11.0 showed that while half-wave potentials were essentially constant, current-concentration ratios were not constant, but decreased with increasing concentration. On this basis together with the data in Table I, it is apparent that the formation of complex units between solvent, buffer and compound is of enough importance so that comparisons of measurements in different buffers are frequently of no value.

By comparing the diffusion coefficient calculated by means of the Ilkovic equation using  $n = 4$  in potassium chloride,  $5.8 \times 10^{-6}$  cm.<sup>2</sup> per sec., with the value  $4.81 \times 10^{-6}$  cm.<sup>2</sup> per sec. found by the Northrop-Anson technique<sup>6</sup> for sodium anthraquinone- $\beta$ -sulfonate in the same medium, it seemed reasonable that four electrons were involved in the reduction and that N-benzyl morpholine was the reduction product. Further experiments are being made to test this point.

(6) Northrop and Anson, *J. Gen. Physiology*, **12**, 543 (1929).

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PRINCETON, NEW JERSEY RECEIVED MARCH 15, 1947

## The Uronic Acid Component of Mucoitinsulfuric Acid

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Sulfuric acid, acetic acid and D-glucosamine have been identified as hydrolytic products of the various types of mucoitinsulfuric acids.<sup>1,2</sup> By analytical methods a uronic acid is readily detectable as a further component but its exact nature has not been precisely determined. Levene and López-Suárez,<sup>3</sup> by oxidative hydrolysis with nitric acid of the funis mucoitinsulfuric acid (from the Whartonian jelly of umbilical cords) isolated a crystalline potassium salt of saccharic acid for which they recorded a potassium analysis but no optical rotation. Such a reaction is not diagnostic for glucuronic acid, since glucose itself gives saccharic acid on nitric acid oxidation. We report herein the exact identification by an unequivocal method, of D-glucuronic acid as the uronic acid component of the mucoitinsulfuric acid from pig gastric mucosa. This was accomplished by application of the previously reported<sup>4</sup> procedure of oxidative hydrolysis with sulfuric acid and bromine. D-Glucosaccharic acid was isolated from

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(1) P. A. Levene, "Hexosamines and Mucoproteins," Longmans, Green and Co., London, 1925.

(2) M. Stacey, *Advances in Carbohydrate Chem.*, **2**, 161 (1946).

(3) P. A. Levene and J. López-Suárez, *J. Biol. Chem.*, **36**, 115 (1918).

(4) M. L. Wolfrom and F. A. H. Rice, *THIS JOURNAL*, **68**, 532 (1946).

the reaction mixture as its crystalline potassium acid salt, identified by analysis and optical rotation. Under similar but non-oxidative hydrolytic conditions, no D-glucosaccharic acid was isolable.

### Experimental

The sodium mucoitinsulfate (S, 6.06%) employed in this work was prepared from commercial pig gastric mucin and was the same material for which extensive analytical data have already been reported.<sup>5</sup> An amount of 1.00 g. of this substance was dissolved at 0° in a mixture of 5 ml. of concentrated sulfuric acid (sp. gr. at 15.56°/15.56° 1.84), 2 ml. of water and sufficient bromine to saturate the solution. The temperature of the reaction mixture was maintained at 0° for four days. Further quantities of bromine were added at intervals to maintain it in excess. After aeration to remove bromine, the mixture was poured slowly onto 200 ml. of ice and water and the sulfuric acid was neutralized in the cold by the addition of solid barium carbonate. The precipitated barium sulfate was removed by filtration and triturated with 20 ml. of 1% aqueous potassium hydroxide and again filtered. The combined filtrates were neutralized with acetic acid and concentrated under reduced pressure at 30–40° to yield a sirup. The sirup was treated with 50 ml. of a 1% solution of hydrogen chloride in methanol, filtered and concentrated under reduced pressure to a sirup. This sirup was extracted with 15 ml. of absolute ethanol, filtered and the solvent removed under reduced pressure. The residual sirup was dissolved in 2 ml. of water and the solution neutralized to ca. pH 7 with solid potassium bicarbonate. After the addition of 2 ml. of glacial acetic acid the solution was allowed to stand overnight in the icebox. Crystals formed that had the characteristic appearance of potassium acid saccharate when viewed under the microscope. These were removed by filtration and recrystallized by dissolving in 1 ml. of aqueous potassium bicarbonate (calcd. amt.) and adding an equal volume of glacial acetic acid; yield 48 mg.,  $[\alpha]^{20}_D + 10^\circ$  (*c*, 1.9 as dipotassium salt). The optical rotation was determined by solution in water containing an equivalent (to phenolphthalein) quantity of potassium bicarbonate and was in agreement with the value,  $[\alpha]^{20}_D + 10^\circ$ , previously found<sup>4</sup> for potassium D-glucosaccharate when polarized under like conditions.

*Anal.* Calcd. for C<sub>6</sub>H<sub>8</sub>O<sub>8</sub>K: K, 15.75. Found: K, 15.72.

The crystalline material was therefore identified as potassium acid D-glucosaccharate.

On repeating the above described hydrolysis of sodium mucoitinsulfate, but omitting the bromine, no potassium acid D-glucosaccharate was isolable.

(5) M. L. Wolfrom, D. I. Weisblat, J. V. Karabinos, W. H. McNeely and J. McLean, *ibid.*, **65**, 2077 (1943).

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RECEIVED MARCH 3, 1947

## NEW COMPOUNDS

### Methyl Isoselenourea Sulfate<sup>1</sup>

To 50 ml. of a 25% solution of cyanamide (kindly supplied by the American Cyanamid Company) 2–3 drops of 12 M hydrochloric acid were added and a current of hydrogen selenide passed through the solution until the selenourea began to crystallize. The selenourea solution was cooled in an ice-bath and the compound filtered and

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