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 *p*H 4.0, phosphate buffer of *p*H 8, and borate buffer of *p*H 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, 5.8×10^{-6} cm.^{2} per sec., with the value 4.81×10^{-6} cm.^{2} per sec. found by the Northrop–Anson technique[6] for sodium anthraquinone-β-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.

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

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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.[1,2] 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,[3] 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[4] procedure of oxidative hydrolysis with sulfuric acid and bromine. D-Glucosaccharic acid was isolated from 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.[5] 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.* *p*H 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., $[\alpha]^{24}\mathrm{D}$ + 10° (*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, $[\alpha]^{20}\mathrm{D}$ + 10°, previously found[4] for potassium D-glucosaccharate when polarized under like conditions.

Anal. Calcd. for $C_6H_9O_8K$: 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.

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* Research Foundation Fellow of the Graduate School.

(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).

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

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NEW COMPOUNDS

Methyl Isoselenourea Sulfate[1]

To 50 ml. of a 25% solution of cyanimide (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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[1] Published by permission of the Director, North Dakota Agricultural Experiment Station.

stored in a vacuum until used. To 185 g. of selenourea (m. p. 198, 22.57% N (calcd. 22.77)) 50 ml. of water was added, the air in the flask displaced with a stream of nitrogen and 103 g. of dimethyl sulfate added in a similar manner as used in the preparation of methyl isothiourea sulfate.[2,3] After the initial reaction subsided the contents were heated with a low flame for twenty-five minutes. The contents of the flask set to a solid dark mass (color due to metallic selenium) before the heating was discontinued. After cooling, the solid mass was washed with 150 ml. of cold ethanol.

The compound was dissolved in about one liter of hot water (4–5 drops of 18 *M* sulfuric acid added) and the metallic selenium, which cleaved in the initial reaction, removed by filtering through a steam jacketed funnel. Methyl isoselenourea sulfate $((\mathrm{H_2N}\overset{\mathrm{SeCH_3}}{\overset{|}{\mathrm{C}}}{=}\mathrm{NH})_2\mathrm{H_2SO_4})$ crystallized on cooling. The first crop yielded 194 g. By reducing the volume to about 100 ml. at reduced pressure and addition of an equal volume of ethanol, an additional 42 g. was obtained. The yield was about 85%. The recrystallized compound melted at 205–207°.

Anal. Calcd. for $C_4H_{14}O_4N_4SSe_2$; N, 15.06; S, 8.61; Se, 42.43. Found: N, 15.12; S, 8.6; Se, 42.4.

When methyl isoselenourea sulfate was hydrolyzed with sodium hydroxide it did not give a good yield of methyl selenomercaptan, as expected from the behavior of the sulfur derivative.[2,4] The principal reaction product was a yellow oil which remained in the reaction mixture.

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(2) Arndt, *Ber.*, **54**, 2236 (1921).

(3) Shildneck and Windus, "Organic Syntheses," **12**, 52 (1932).

(4) Windus and Shildneck, *ibid.*, **14**, 54 (1934).

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Some New Selenium Ethers[1]

β-Hydroxyethyl Phenyl Selenide

After the air in a flask containing 350 ml. of absolute ethanol was displaced by nitrogen, 103 g. (²/₃ mole) of phenyl selenomercaptan were added. An equivalent of sodium was then added in small pieces until dissolved. The flask was immersed in ice water and 84 g. of ethylene bromohydrin were added over a period of about five minutes. The reaction was quite vigorous. After cooling to room temperature a few drops of 12 *M* hydrochloric acid were added and a current of air was drawn through the solution to oxidize any unreacted phenylselenomercaptan to the diselenide. The salt was filtered, washed with dry ether and the solution distilled *in vacuo*. The product collected at 152–156° at 18 mm. was redistilled. The fraction distilling at 152–153° at 16 mm. was 116 g., 87% of theoretical.

Anal. Calcd. for $C_8H_{10}OSe$: Se, 39.26. Found: Se, 38.6.

When brominated in carbon tetrachloride an orange compound melting at 113° was obtained. The compound was unstable and therefore was not successfully recrystallized.

Anal. Calcd. for $C_8H_{10}OBr_2Se$: Se, 21.88; Br, 44.28. Found: Se, 22.9; Br, 43.8.

β-Hydroxyethyl Benzyl Selenide

This compound was prepared from sodium benzyl selenide[2] and ethylene bromohydrin by the same procedure as for β-hydroxyethyl phenyl selenide except the volume of alcohol per mole of sodium benzyl selenide was twice that used for the phenyl derivative. The compound distilled at 130–132° at 2 mm. The yield was about 70%.

Anal. Calcd. for $C_9H_{12}OSe$: Se, 36.70. Found: Se, 36.5.

The compound gave an unstable bromine addition product.

β-(Phenylseleno)-diethylacetyl

To 25 ml. of absolute ethanol, 15.7 g. (0.1 mole) of freshly distilled phenylselenomercaptan were added. The flask was cooled and after 2.3 g. of sodium (added in small pieces) were dissolved, 16 g. of β-chloro diethylacetal were added dropwise. The reaction mixture was warmed and refluxed gently for one hour. The flask was cooled and the contents were poured into 300 ml. of water. The water was made alkaline with sodium hydroxide. The lower layer, the acetal, was taken up in ether and the water was extracted with ether. The combined ether solutions were dried over anhydrous sodium sulfate and distilled at reduced pressure. β-Phenylselenodiethylacetal, b. p. 153–155° at 17 mm., straw yellow color, was obtained in 60% yield. When redistilled nearly all the product was collected at 153–153.5° at 17 mm.

Anal. Calcd. for $C_{12}H_{18}O_2Se$: Se, 28.90. Found: Se, 28.7.

The acetal gave an unstable bromine addition compound of orange yellow crystals. After hydrolyzing the acetal with *N* sulfuric acid, the aldehyde was treated with ammonia and hydrogen cyanide and the amino nitrile hydrolyzed with hydrochloric acid. The amino acid, β-(phenylseleno)-alanine,[2] was isolated in a yield of about 10% based on the acetal.

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(1) Published by permission of the Director, North Dakota Agriculture Experimental Station.

(2) Painter, THIS JOURNAL, **69**, 229 (1947).