Reaction with Ammonia.—β-Sulfopropionic anhydride was added in small portions to a large excess of liquid ammonia. After removal of the ammonia by evaporation, the white crystalline material was warmed gently to 60° to remove the last traces of ammonia and crystallized from 80% methanol. The crystallized product melted at 179°. It was identified as the ammonium salt of β-sulfopropionamide by its reactions and analysis.

Anal. Calcd. for $C_3H_{10}O_4H_2S$ ($NH_4{}^{+}{}^{-}O_3SCH_2CH_2CONH_2$): N, 16.45. Found: N, 16.50.

Reaction with Methyl Alcohol.—β-Sulfopropionic anhydride was treated with a slight excess of anhydrous methanol and the excess then removed in a vacuum desiccator over phosphorus pentoxide. A crystalline highly hygroscopic material was obtained. The melting point of this substance was 73°.

Anal. Calcd. for $C_4H_8O_5S$ ($HO_3SCH_2CH_2COOCH_3$): S, 19.1; neut. equiv., 168. Found: S, 18.9; neut. equiv., 162.

Proof that the carboxylic acid group is esterified in this molecule and the sulfonic acid group is free was established in a manner similar to that described for the anilide. A 0.02 *N* solution of the ester was prepared and the *p*H determined immediately.[9] The value obtained, 2.05, indicates that the free acid group is highly ionized. It is concluded therefore that the sulfonic acid group must be free.

Summary

1. Sulfuryl chloride reacts with aliphatic carboxylic acids in the presence of actinic light to yield sulfonated derivatives.

2. The lower aliphatic acids (propionic, isobutyric, butyric) yield cyclic sulfocarboxylic anhydrides in which the sulfo groups are in the beta or beta and gamma positions, while the higher aliphatic acids (valeric, hexahydrobenzoic, lauric) yield sulfonyl chlorides indicative of substitution in positions other than beta and gamma.

3. The reactions of the sulfoacid anhydrides with alcohols, ammonia and amines have been investigated.

4. A chain mechanism involving chlorine atoms and organic free radicals is suggested to explain the photochemical sulfonation of aliphatic compounds.

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[9] The ester hydrolyzes rather rapidly in aqueous solution.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE STATE UNIVERSITY OF IOWA]

Preparation and Properties of Derivatives of Inositol*

BY FOREST A. HOGLAN AND EDWARD BARTOW

Hoglan and Bartow[1] prepared inositol in large quantities cheaply from calcium phytate, the precipitate made by adding lime to starch factory steep water. They used hydrolysis without acid or alkali and obtained 9 to 12 lb. of inositol for each 100 lb. of starting material.

Having made several new esters of inositol,[1] the authors have continued the study of inositol and derivatives.

Experimental Procedure

Preparation of Inositol.—Better calcium phytate was obtained from light steep water than from heavy steep water. To determine which was the better, calcium phytate was precipitated from both light and heavy steep water and each was treated as described by Bartow and Walker[2] except that hydrolysis was carried out in three shallow metal containers instead of 21 jars. These containers, each 60 cm. deep, were made from 30 gallon (190 liter) gasoline drums by cutting out the center portion and using the ends as containers. These containers eliminated excessive handling, obviated any loss of material due to breakage, and yet provided the uniform heat distribution required for hydrolysis. In each experiment about 225 kg. of the wet precipitate, which was equivalent to about 40 kg. of dry phytin, was hydrolyzed by heating in an autoclave for ten hours under 5.6 sq. cm. steam gage pressure. 9.5% of inositol was obtained from the light steep water precipitate and 8.1% from the heavy steep water precipitate. The light steep water precipitate gave a product of higher purity. The inositol obtained from heavy steep water precipitate contained considerable protein material and was very difficult to purify.

Oxidation of Inositol with Nitric Acid.—Previous investigators[2,3,4] have oxidized inositol with concentrated or fuming nitric acid, dried the oxidized product until free from nitric acid, and neutralized a water solution of the oxidized product with sodium bicarbonate or potassium bicarbonate, obtaining salts of tetrahydroxyquinone, green crystalline compounds. By neutralizing with sodium and potassium carbonates, they obtained violet colored crystalline compounds which they called rhodizonates. The authors have thus far been unable to distinguish tetrahydroxyquinone from rhodizonic acid.

Inositol has been oxidized under various conditions and various concentrations of nitric acid and the products have been used in the preparation and study of derivatives.

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[1] F. Hoglan and E. Bartow, *Ind. Eng. Chem.*, **31**, 749–750 (1939).

[2] E. Bartow and W. W. Walker, *ibid.*, **30**, 300–303 (1938).

[3] O. Gelormini and N. Artz, THIS JOURNAL, **52**, 2483 (1930).

[4] M. Maquenne, *Compt. rend.*, **104**, 297 (1887).

Preparation of Sodium Tetrahydroxyquinone.—Sodium tetrahydroxyquinone was prepared by oxidizing inositol at temperatures varying from 55 to 80°, according to the method of Gelormini and Artz[3] (Table I). At the higher temperatures (80°) the oxidized product usually turned dark when nearly dry, but yielded sodium tetrahydroxyquinone of good quality. The yield of pure sodium tetrahydroxyquinone from four experiments (Table I) ranged from 28 to 40% of the weight of inositol used. A larger yield (Expt. 66) was obtained when excess sodium bicarbonate was added but the product was of poor quality.

TABLE I

OXIDATION OF INOSITOL WITH FUMING NITRIC ACID AT DIFFERENT TEMPERATURES

Expt.	Oxidation temp., °C.	Yield of sodium tetrahydroxyquinone, % of inositol used
46	80	36
47	80	40
57	65	32
58	60	28
66	55	60

The following procedure using concentrated nitric acid (sp. gr. 1.42) instead of fuming nitric acid (sp. gr. 1.56) gave better results, since the reaction is less violent and it is unnecessary to control the temperature of oxidation.

Suspend inositol (100 g.) in four times its weight of concentrated nitric acid (sp. gr. 1.42) in an open dish and allow the mixture to oxidize slowly overnight at room temperature. Warm the green colored, partially oxidized product carefully over a steam-bath. When the sirupy product begins to thicken, stir frequently to permit escape of the oxides of nitrogen. Continue the heating until a white or slightly brown solid is obtained. To obtain sodium tetrahydroxyquinone, dissolve this product in five times its weight of distilled water, filter to remove undissolved matter, and add sodium bicarbonate to the filtrate until no more effervescence occurs on addition of a new portion. The yield is 35–40% of pure sodium tetrahydroxyquinone from the original inositol.

Preparation of Potassium Salts from Oxidized Inositol.—To prepare the product described by Gelormini and Artz[3] and others, as potassium rhodizonate, dissolve oxidized inositol in five times its weight of distilled water and warm the solution carefully on a steam-bath. Add a saturated solution of potassium carbonate slowly, a small amount at a time. Add a new portion only when effervescence has ceased. When the solution is nearly neutralized, sparkling reddish-violet colored crystals begin to settle out. Stir for about two hours and separate the crystals by filtration, wash well with distilled water, and finally with alcohol. The product obtained is identical with that prepared and described by Gelormini and Artz.[3]

The same compound was obtained by using potassium acid carbonate (instead of potassium carbonate) to neutralize the oxidized inositol solution. The reaction proceeded in the same manner as just described and the product obtained was identical with the potassium salt obtained when potassium carbonate was used as a neutralizing agent.

Comparison of Tetrahydroxyquinone and Rhodizonic Acid.—It did not seem likely that a sodium derivative of tetrahydroxyquinone and a potassium derivative of rhodizonic acid could be made from the same oxidation product, or that different states of oxidation would be obtained when sodium or potassium carbonates or acid carbonates were used. Experiments were therefore made to determine whether the potassium salts were of one acid (rhodizonic acid) and the sodium salts were of a different acid (tetrahydroxyquinone) as stated by Gelormini and Artz.[3]

Neutralization of a water solution of oxidized inositol with sodium carbonate or sodium bicarbonate yielded glistening green salts identical in appearance.

Neutralization of a water solution of oxidized inositol with potassium bicarbonate or potassium carbonate yielded violet colored salts, identical in appearance but different from the sodium salts. All four compounds had the same color when pulverized.

The same derivative was obtained from both the sodium and potassium salts when treated in the following manner. The salts were treated with dilute hydrochloric acid in a manner described by Nietzki and Benckiser.[5] In each case bluish-black crystals settled out on cooling and when filtered, washed, and dried, had the same appearance.

Each of these products was benzoylated by boiling with a slight excess of benzoyl chloride in a manner described by Nietzki and Kehrmann.[6] In each case a brisk reaction took place before the boiling point of benzoyl chloride was reached, and fumes of hydrogen chloride were given off. On cooling, yellow precipitates formed which when filtered, dried and recrystallized, gave yellow nicely crystalline compounds which were identical in appearance.

The benzoyl esters prepared from the sodium and potassium salts melted and decomposed at the same temperature, 266–270°, indicating that the sodium and the potassium salts were derivatives of the same compound, either of tetrahydroxyquinone or rhodizonic acid.

Amine Derivatives of Tetrahydroxyquinone.—A derivative of tetrahydroxyquinone and aniline was prepared according to the method of Nietzki and Schmidt.[7] The red crystals obtained were washed with denatured alcohol which in no way changed their appearance, but washed with water the red color immediately changed to a bright glistening green. After two or three washings with water they were again washed with denatured alcohol and finally dried. By analysis this compound was shown to be an addition product of two molecules of aniline and one molecule of *tetrahydroxyquinone* (Table II, 1).

It was unnecessary to use free tetrahydroxyquinone to prepare the aniline derivative. The same derivative was obtained by suspending sodium tetrahydroxyquinone in dilute (50%) alcohol and adding concentrated hydrochloric acid until all the sodium tetrahydroxyquinone was dissolved, avoiding an excess of acid, filtering and adding slowly with stirring an excess of aniline dissolved in dilute (50%) alcohol. Crystals formed immediately and when a large excess of aniline had been added, they appeared orange colored with a greenish glisten. The product was filtered, washed repeatedly with alcohol, and when washed with water the crystals remaining on the filter were bright green in color. After washing again with alcohol the prod-

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(5) R. Nietzki and Th. Benckiser, *Ber.*, **18**, 1833–1843 (1885).

(6) R. Nietzki and Fr. Kehrmann, *ibid.*, **20**, 3152 (1887).

(7) R. Nietzki and A. W. Schmidt, *ibid.*, **21**, 1855 (1888).

uct was dried and nitrogen determined (Table II, 1a). The composition was the same as when free tetrahydroxyquinone was used.

Other Amine Derivatives of Tetrahydroxyquinone.—Tetrahydroxyquinone derivatives of ortho, meta and para toluidine were prepared by the action of the toluidines on sodium tetrahydroxyquinone in the manner just described. The percentage of nitrogen (Table II, 2, 3, 4) indicates that each derivative is a combination of two molecules of the toluene and one molecule of tetrahydroxyquinone.

The variation in color of the derivatives obtained (Table II) from ortho, meta, and para toluidine, is evidently due to the position occupied by the group which is substituted in the aniline molecule.

To further investigate color relationships and variations of the ortho, meta, and para substituted amine derivatives of tetrahydroxyquinone, additional amine derivatives were prepared by the method used for the preparation of aniline derivatives with sodium tetrahydroxyquinone.

In cases where derivatives were obtained, crystal formation began soon after addition of the amine was begun. An excess of the amine was added in each case to assure completeness of reaction. After stirring for about two hours, the derivatives were separated by filtration, washed several times with 95% alcohol, repeatedly with distilled water, again with 95% alcohol, and dried *in vacuo*. The analyses (Table II) indicate the derivatives obtained are addition products in which two molecules of the amine are combined with one molecule of tetrahydroxyquinone.

The derivatives of *p*-toluidine, *p*-chloroaniline, and *p*-bromoaniline were bright green in color and identical in appearance. The derivatives of *m*-toluidine, *m*-chloroaniline, and *m*-bromoaniline were orange in color instead of green as in the para compounds. Only one ortho substituted amine derivative (*o*-toluidine) was obtained and no color comparison of ortho derivatives could be made.

The *o*-toluidine derivative was prepared without difficulty but no compound was obtained either from *o*-chloroaniline or *o*-bromoaniline.

The presence of the nitro group in the aniline molecule also seems to inhibit reaction with tetrahydroxyquinone since no compound was formed with either ortho, meta, or para nitroaniline.

TABLE II

AMINE DERIVATIVES OF TETRAHYDROXYQUINONE

	Amine used	Color of derivative	Nitrogen % Theoretical	Found	
1	Aniline (using free tetrahydroxyquinone)	Green	7.85	7.74	8.05
1a	Aniline (using sodium tetrahydroxyquinone)	Green	7.85	7.73	7.97
2	*o*-Toluidine	Brown	7.25	6.99	6.58
3	*m*-Toluidine	Orange	7.25	7.22	6.81
4	*p*-Toluidine	Green	7.25	7.10	7.02
5	*o*-Chloroaniline (no reaction)				
6	*m*-Chloroaniline	Orange	6.65	6.80	6.90
7	*p*-Chloroaniline	Green	6.65	6.45	6.44
8	*o*-Bromoaniline (no reaction)				
9	*m*-Bromoaniline	Orange	5.50	5.54	5.65
10	*p*-Bromoaniline	Green	5.50		
11	*o*-Nitroaniline (no reaction)				
12	*m*-Nitroaniline (no reaction)				
13	*p*-Nitroaniline (no reaction)				
14	*o*-Aminophenol (no reaction)				

Esters of Tetrahydroxyquinone.—In addition to the benzoyl ester of tetrahydroxyquinone previously described, several new esters of the fatty acid series were prepared. In each case, tetrahydroxyquinone was suspended in an excess of the acid chloride used and the flask connected to a reflux condenser and carefully heated on an oil-bath. A brisk reaction started at a temperature of about 60° and hydrogen chloride fumes were given off freely in each case. As the reaction proceeded, the suspended tetrahydroxyquinone disappeared, the mixture became dark colored, and the impure, yellow colored ester settled out. When the reaction had subsided the temperature was slowly raised to the boiling point of the acid chloride. After two hours the flask was removed from the oil-bath, cooled, and the contents poured with vigorous stirring into a cold dilute sodium carbonate solution. A dark oily layer formed on the surface of the liquid and after prolonged stirring the oily layer began to solidify. After standing for two hours, the dark colored spongy solid was separated by filtration and washed repeatedly with cold water. Excess acid and other impurities were removed by washing the precipitate several times with cold alcohol or an alcohol–water mixture. Washing with alcohol removed much of the dark coloring matter leaving the ester in most cases in fairly pure form. Recrystallization gave pure products. All of the esters prepared were bright yellow and nicely crystalline, and melted with decomposition (Table III).

TABLE III

ESTERS OF TETRAHYDROXYQUINONE

	Ester of tetrahydroxyquinone	M. p., °C.	
1	Propionyl	231	dec.
2	Butyryl	237	dec.
3	Isobutyryl	121	
4	Valeryl	241	dec.
5	Isovaleryl	218	dec.
6	Isocaproyl	222–5	dec.
7	Caprylyl	224	dec.
8	Capryl	208–11	dec.
9	Benzoyl	266–70	dec.

Because of the high solubility of the propionyl, *n*-butyryl, isobutyryl, valeryl and isovaleryl esters, these compounds were recrystallized from dilute alcohol. The isocaproyl, caprylyl and capryl esters were recrystallized from 95% alcohol. Because of the extreme insolubility of the benzoyl ester in alcohol and other solvents, it was recrystallized from boiling benzoyl chloride.

Metallic Salts of Tetrahydroxyquinone.—In view of the unusual colors and slight solubility of the potassium, sodium and barium salts of tetrahydroxyquinone, or rhodizonic acid, a number of new salts of the common metals have been prepared. Lithium and ammonium derivatives were prepared by the action of the soluble bicarbonates on a solution of oxidized inositol according to the procedure described for the preparation of sodium tetrahydroxyquinone. Lithium tetrahydroxyquinone crystallized in glistening green crystals similar in appearance to the sodium salt previously described. The ammonium salt crystallized in brown needles.

Since the colors of the metallic derivatives might have significance in qualitative analysis, the metals included in "The Iowa System of Qualitative Analysis" were selected and salts of tetrahydroxyquinone prepared from them by dissolving tetrahydroxyquinone in distilled water and adding, with stirring, an excess of a solution of the metallic chloride, nitrate or acetate. In most cases the metallic salt of tetrahydroxyquinone formed and precipitated immediately, but in a few cases it was necessary to make a solution slightly alkaline before precipitation occurred. Stirring was continued in each case for one to two hours and the mixture allowed to stand an additional two hours. The metallic salts of tetrahydroxyquinone settled out leaving a clear colorless liquid, instead of the colored tetrahydroxyquinone solution, above the precipitate. The precipitate in each case was washed with water, dried and pulverized. Twenty-one metallic salts were prepared from tetrahydroxyquinone (Table IV).

TABLE IV

COLOR OF METALLIC SALTS OF TETRAHYDROXYQUINONE

Metallic salt (of tetrahydroxyquinone)	Color of pulverized salt
Lead	Deep purple
Silver	Green
Mercury	Green
Barium	Bright red
Calcium	Brown
Bismuth	Brownish-black
Iron	Black
Copper	Nearly black
Cobalt	Reddish-brown
Nickel	Dark brown
Cadmium	Reddish-brown
Zinc	Deep red
Antimony	Dark brown
Tin	Reddish-brown
Manganese	Dark brown
Magnesium	Reddish-brown
Aluminum	Reddish
Chromium	Green
Lithium	Green (glistening)
Ammonium	Brown
Sodium	Reddish-brown (green when pulverized)
Potassium	Reddish-brown

The salts, except lithium, did not show definite crystalline form. Most of these salts showed color variations which apparently were due to the conditions of the reaction and the amounts of reagents used. Study to determine the composition of these compounds is desirable.

Conclusions

1. Sufficient inositol for use in research was prepared from the lime precipitate obtained from the dilute acid solution in which corn had been soaked in manufacturing starch.

2. Lime precipitate obtained from light steep water is the most suitable material for production of inositol.

3. Sodium and potassium salts of tetrahydroxyquinone were prepared in quantity from oxidized inositol and used for further research.

4. The same compound is obtained when sodium tetrahydroxyquinone and potassium rhodizonate are treated with hydrochloric acid. This compound has all the properties of tetrahydroxyquinone as described by Nietzki and Benckiser.[5]

5. Tetrahydroxyquinone combines with aniline and some of its derivatives to give highly colored addition products. The position (ortho, meta and para) substituted in the aniline molecule apparently determines the color of the addition product.

6. A new series of esters of tetrahydroxyquinone and the fatty acids are yellow in color and decompose at their melting points.

7. Several new metallic salts of tetrahydroxyquinone were prepared. Study of the composition and properties of these compounds is desirable.

IOWA CITY, IOWA

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