

Hydrogen Peroxide Color Reactions with Anthocyanins.—The anthocyanins were prepared by the following method: Samples of the finely ground plant material were extracted with 5 volumes of 95% ethyl alcohol by boiling for three minutes. The filtered extracts were evaporated in vacuum. 200-mg. samples of the crude materials were dissolved in 5 cc. of ethyl alcohol containing 0.5 cc. of *N* HCl. The solution was centrifuged and a small amount of insoluble matter was discarded. From the alcoholic solution the anthocyanins were precipitated with a large excess of ether. The precipitated anthocyanin chlorides were re-dissolved in alcohol and again precipitated with ether and dried in vacuum.

In the following is described in detail the hydrogen peroxide-sodium hydroxide color reaction as given by the anthocyanin of red beet: To 2.5 mg. of the pigment in 0.5 cc. of 50% ethyl alcohol was added 0.3 cc. of 3% hydrogen peroxide. The mixture was agitated for one minute. On addition of 0.3 cc. of 0.2 *N* sodium hydroxide the color turned reddish-violet and on addition of 0.5 cc. of 0.2 *N* sulfuric acid the solution became red. The red pigment was fairly stable in acid solution. In the control tube in which water was used instead of hydrogen peroxide a yellow color was formed. In Table II are recorded a series of color reactions as given by other pigments. The carotenoids physalinen, capsanthin, and cryptoxanthin (not listed in Table II) gave no color under similar conditions.

Color Reactions with Other Pigments.—With other pigments the technique of the reaction was carried out in the same manner. In the controls water was used instead of hydrogen peroxide. The results are summarized in Table II. The color reaction may also be carried out directly on the alcoholic extracts of plants. In the case of molds the ether extracts of the media to which some water is added may be employed.

For the tests on flavanols 0.5 cc. of the alcoholic extracts of the flowers were used. Penicillin and actinomycin³ were very kindly furnished by Merck and Company, Inc. For the pure carotenoids we are grateful to Dr. L. Zechmeister of the California Institute of Technology.

Color Reactions with Polyphenols.—Compounds containing phenolic groups in positions 3 and 5 readily give color reactions at room temperature with 3% peroxide and 0.2 *N* sodium hydroxide. Thus phloroglucinol (1 mg. in 0.5 cc. 95% ethyl alcohol) gives a violet color and orcinol gives a pink color. Phenol, catechol, resorcinol, thymol, salicylic acid and cresol give no color. Hydroquinone and pyrogallol give a yellow color, being directly affected by the alkali. Substances of a quinone structure and having one phenolic group like citrinin apparently undergo certain oxidative changes by hydrogen peroxide treatment, which make the intense and rapid color reaction possible.

In the case of phloroglucinol maximum color formation (intense violet) takes place two to three minutes after the addition of sodium hydroxide. Then the intensity of the color gradually decreases and the solution becomes colorless. On slight heating, however, maximum color intensity is obtained immediately. At the beginning of the reaction

the color is reversible. The case is similar with the color forming pigments.

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NEW YORK, N. Y.

RECEIVED DECEMBER 21, 1942

The Conductance of Aqueous Solutions of Magnesium Perchlorate

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In the course of some investigations on non-aqueous solutions of magnesium perchlorate, of which the remarkably high solubilities in various organic solvents were measured by Willard and Smith,¹ we noticed that no conductance data were available for the aqueous solutions of this salt. These we therefore determined for the range of concentrations from 0.001 equivalent per liter to saturation (6.588 equivalents per liter¹). Several series of solutions were prepared, some with the anhydrous salt, some with the hexahydrate as obtained from the G. F. Smith Co., some with carefully recrystallized hexahydrate derived from G. F. Smith anhydrous salt. All solutions were prepared in calibrated glassware, successive dilutions being carried out on a weight basis with the usual buoyancy corrections. A Washburn conductivity cell was used with an oil thermostat kept at 25°. A Wolff potentiometer-Wheatstone bridge combination of high precision² was used, the alternating current being provided by a microphone hummer and, in part of the work, by an R. C. A. beat-frequency audio oscillator. Conductivity water of specific conductance of less than 10⁻⁶ mho was used throughout. Table I gives the equivalent conductances interpolated for the series of round concentrations

TABLE I
CONDUCTANCES OF AQUEOUS SOLUTIONS OF MAGNESIUM PERCHLORATE AT 25°

Concentrations, equivalents per liter	Equivalent conductances in mhos	Concentrations, equivalents per liter	Equivalent conductances in mhos
0	(128.5)	0.5	79.4
0.001	120.8	0.7	75.7
.002	118.2	1.0	71.0
.005	112.6	2	59.1
.01	108.0	3	49.4
.02	103.9	4	40.5
.05	98.3	5	31.4
.07	95.7	6	22.6
.1	93.1	6.588	17.5
.2	87.4		

(1) H. H. Willard and G. F. Smith, *THIS JOURNAL*, **46**, 286 (1923).

(2) O. Wolff, *Z. Instrumentenkunde*, **21**, 227 (1901); **22**, 224 (1902); etc.

(3) S. A. Waksman and M. Tishler, *J. Biol. Chem.*, **142**, 519 (1942).

usual in the "I. C. T." The limiting conductance of 128.5 is a tentative value based on the ionic mobilities and their temperature coefficients given in the Landolt-Börnstein-Roth tables. The accuracy of the measured equivalent conductances is within 0.1 conductance unit, except below the concentration 0.01 equivalent per liter where the accuracy is within 0.5 conductance unit.

This work is part of a project supported by the General Research Council of the Oregon State System of Higher Education to which the authors express their gratitude.

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RECEIVED JANUARY 12, 1943

NEW COMPOUNDS

Derivatives of 2,5-Diaminobenzenesulfonamide

The compounds reported below were made as part of a study of toxicology of *p*-phenylenediamine derivatives. Improved syntheses of intermediates are also reported.

2-Chloro-5-nitrobenzenesulfonyl Chloride.¹—One mole of *p*-nitrochlorobenzene and 5 moles of chlorosulfonic acid were heated for twelve hours at 120–130°. The reaction mixture was cooled, poured on ice, the product filtered, pressed dry and crystallized from carbon tetrachloride (10 g. of solid to 25 ml. of carbon tetrachloride); 55% yield of a product, m. p. 85–87°, was obtained.

2-Chloro-5-nitrobenzenesulfonamide.¹—The nitrochlorobenzenesulfonyl chloride was added slowly to a large excess of cold 28% ammonia solution with good stirring. The strongly exothermic reaction was cooled externally. The mixture was allowed to stand overnight, steam distilled and an 89% yield of a product, m. p. 184–185°, was obtained.

2-Amino-5-nitrobenzenesulfonamide.²—A mixture of 5 g. of nitrochlorobenzenesulfonamide, 5 g. of ammonium carbonate, 25 ml. of ammonium hydroxide (28%) and 1 g. of cupric sulfate was heated in a sealed glass tube for four hours at 120°. The contents of the tube were evaporated slowly to remove excess ammonia. The solution, on saturation with sulfur dioxide, gave a yellow precipitate. The product was filtered and recrystallized from aqueous alcohol. The yield was 86%, m. p. 208°.

2,5-Diaminobenzenesulfonamide.²—Nitroaminobenzenesulfonamide was dissolved in excess alkali and reduced with 3 moles of sodium hydrosulfite. The crude product was crystallized from water. The yield was 70%, m. p. 184°.

Anal. Calcd. for $C_6H_9O_2N_3S$: N, 22.41. Found: N, 22.41, 22.40.

(1) P. Fischer, *Ber.*, **24**, 3194 (1891); Claus and Mann, *Ann.*, **265**, 88 (1891).

(2) P. Fischer, *Ber.*, **24**, 3790 (1891).

2-Anilino-5-nitrobenzenesulfonamide.³—Nitrochlorobenzenesulfonamide was refluxed with excess aniline in the presence of excess calcium carbonate in an atmosphere of carbon dioxide for two and one-half hours. The mixture was cooled. Excess aniline was steam distilled. The residue was purified by crystallization from alcohol. The yield was 75%, m. p. 168–169°.

2-Anilino-5-aminobenzenesulfonamide.—2-Anilino-5-nitrobenzenesulfonamide was reduced in two ways (a) with alkaline hydrosulfite a 74% yield of a product, m. p. 164° (crystallized from 80% alcohol) was obtained. (b) Catalytic reduction in alcoholic solution in the presence of Raney nickel catalyst gave 88% yield of a product, m. p. 164°.

Anal. Calcd. for $C_{12}H_{13}O_2N_3S$: N, 15.98. Found: N, 15.85, 16.00.

2-Chloro-5-nitrobenzenesulfonethanolamide.⁴—Nitrochlorobenzenesulfonyl chloride was slowly added to a cooled mixture of excess monoethanolamine (35% aqueous solution) containing 3% potassium hydroxide. Stirring was continued after removal of the ice-bath until the reaction mixture reached room temperature. The mixture was acidified with hydrochloric acid, and filtered. The product was crystallized from either water or isopropanol. The yield was 58%; m. p. 133–135°.

Anal. Calcd. for $C_8H_9O_2N_2ClS$: N, 9.96; Cl, 12.80. Found: N, 9.90; Cl, 12.30.

2-Amino-5-nitrobenzenesulfonethanolamide.—Amination was performed as described above for nitroaminobenzenesulfonamide. The product was a yellow powder; yield 87%; m. p. 149–50°.

Anal. Calcd. for $C_8H_{11}O_2N_3S$: N, 16.00. Found: N, 15.80, 15.85.

2,5-Diaminobenzenesulfonethanolamide.—The nitro-amino compound was reduced catalytically in alcoholic solution using Raney nickel catalyst. The compound, after filtering off the nickel, was isolated as the hydrochloride by passing dry hydrogen chloride into the alcoholic solution and precipitating the compound with ethyl acetate. The yield was 73%, m. p. 184°.

Anal. Calcd. for $C_8H_{14}O_2N_3S \cdot 2HCl$: N, 13.80. Found: N, 13.50, 13.65.

2-(Hydroxyethyl)-amino-5-nitrobenzenesulfonethanolamide.—Nitrochlorobenzenesulfonyl chloride was added to cold monoethanolamine, without cooling; the reaction was exothermic. The mixture was finally warmed on a water-bath for one hour and allowed to stand overnight. Bright yellow needles crystallized from the dark red solution. The product was crystallized from water, m. p. 119–120°; yield 73%.

Anal. Calcd. for $C_{10}H_{15}O_3N_3S$: N, 13.70. Found: N, 13.51, 13.53.

2-(Hydroxyethyl)-amino-5-aminobenzenesulfonethanolamide.—The nitro derivative was reduced with alkaline hydrosulfite in 91% yields; m. p. 162–163° (from alcohol). Catalytic reduction in alcohol solution with Raney nickel catalyst gave an 82% yield.

(3) Ullmann, *ibid.*, **41**, 3746 (1908); P. Fischer, **24**, 3798 (1891).

(4) Swiss Patent 180,578, *Chem. Zentr.*, **107**, 4516 (1936). This compound is mentioned but not described.