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.

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF OREGON
EUGENE, OREGON

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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.

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 $C_8H_9O_5N_2ClS$: 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 $C_8H_{11}O_5N_3S$: N, 16.00. Found: N, 15.80, 15.85.

2,5-Diaminobenzenesulfonethanolamide.—The nitroamino 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 $C_8H_{14}O_3N_3S \cdot 2HCl$: 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 $C_{10}H_{15}O_6N_3S$: 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.

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

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

(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.

Anal. Calcd. for $C_{10}H_{17}O_4N_3S$: N, 15.28. Found: N, 15.25, 15.24.

RESEARCH AND BIOCHEMICAL LABORATORIES
LAWRENCE RICHARD BRUCE, INC. A. R. GOLDFARB
STAMFORD, CONNECTICUT BERNARD BERK

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Ethyl *p*-Aminobenzenesulfonate

Unsuccessful attempts to prepare this compound were described recently.[1] It has been prepared by hydrogenating 5 g. of ethyl *p*-nitrobenzenesulfonate in 150 cc. of absolute ethanol containing 0.8 g. of hydrogen chloride with 0.2 g. of previously reduced Adams PtO_2 catalyst. The reduction, at 30–40 lb. pressure, was complete in ten to thirty minutes. The solution was concentrated *in vacuo* to a volume of 30–50 cc., filtered, and diluted with absolute ether. A crystalline hydrochloride separated. This material was analyzed before it was discovered that the compound was unstable and lost hydrogen chloride spontaneously when dry.

Anal. Calcd. for $C_8H_{12}O_3NSCl$: Cl, 14.92. Found: Cl, 14.33.

The above salt was stirred with ice water and treated with an excess of ice-cold sodium bicarbonate solution.

The oil which separated crystallized on scratching and was triturated with ice water and dried on a porous plate. The yield was 2–3 g. of white crystals, m. p. 78–80°.

Anal. Calcd. for $C_8H_{11}O_3NS$: N, 6.95. Found: N, 7.00.

The compound was unstable and after one week contained only 17.10% ethoxyl, calcd. for 22.39%. A sample three years old decomposed from 160–210° and gave only traces of ethoxyl.

RESEARCH LABORATORY
MALTBIE CHEMICAL CO.
NEWARK, N. J. L. A. WALTER

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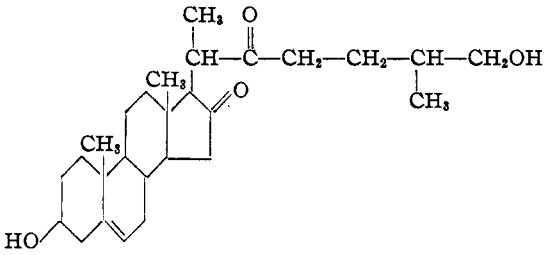
[1] Crossen, Jenkins and Rogers, *Pharm. Arch.*, **12**, 21 (1941).

COMMUNICATIONS TO THE EDITOR

STEROLS. CLIII. SAPOGENINS. LXV. KRYPTOGENIN, A NEW TYPE OF SAPOGENIN FROM *BETH* ROOT

Sir:

In the course of our plant studies we have isolated from *Beth* root a new steroid having the composition $C_{27}H_{42}O_4$, m. p. 187–189°, which we have named kryptogenin. *Anal.* Calcd. for $C_{27}H_{42}O_4$: C, 75.3; H, 9.8. Found: C, 75.1; H, 9.8. Sodium–isopropyl alcohol reduction of this product gave diosgenin isolated as its acetate, m. p. and mixed m. p., 202°. *Anal.* Calcd. for $C_{29}H_{44}O_4$: C, 76.3; H, 9.7. Found: C, 76.2; H, 9.7. Catalytic hydrogenation (Adams catalyst) of kryptogenin in ether containing several drops of acetic acid gave 5,6-dihydrokryptogenin, m. p. 169–171°. *Anal.* Calcd. for $C_{27}H_{44}O_4$: C, 74.9; H, 10.3. Found: C, 74.7; H, 10.1. The latter upon mild oxidation with chromic anhydride in acetic acid gave a good yield of 3-dehydrotigogenoic acid [Marker, Turner and Ulshafer, THIS JOURNAL, **63**, 763 (1941)], m. p. and mixed m. p., 185–187°. *Anal.* Calcd. for $C_{27}H_{40}O_5$: C, 72.9; H, 9.1. Found: C, 73.0; H, 9.1. We have found it to have the following structure:



It is noteworthy that the side chain is distinctly different from but definitely related to the spiroketal structure characteristic of the other steroidal sapogenins. The amounts of the new steroid and of diosgenin [Marker, Turner and Ulshafer, THIS JOURNAL, **62**, 2542, (1940)] in *Beth* root (*Trillium erectum*) are about equal. The details of the work will be published in a forthcoming issue of THIS JOURNAL.

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SCHOOL OF CHEMISTRY AND PHYSICS RUSSELL E. MARKER
THE PENNSYLVANIA STATE COLLEGE R. B. WAGNER
STATE COLLEGE, PENNA. DALE P. J. GOLDSMITH
PAUL R. ULSHAFER
CLARENCE H. RUOF

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