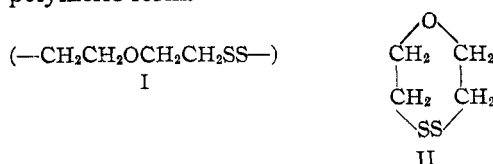


low-molecular weight organic compounds in the distillate. The rate of production of monomer is extremely slow but has not diminished with time, indicating that actually depolymerization is occurring. Addition of small amounts of sodium hydroxide to the polymeric dispersion significantly increases the rate of depolymerization.

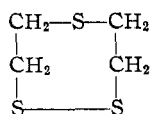
The polymer resulting from the condensation of bis-(2-chloroethyl) ether and sodium disulfide<sup>5</sup> yields a pale yellow oil of characteristic odor. Attempts to distil it have resulted in decomposition. The compound is stable indefinitely if completely dry but water converts it slowly back to the original polymer. Aqueous sodium sulfide or polysulfide converts the oil rapidly to the polymeric form.



The physical properties of the oil were determined and compared with those calculated for structure II.

	Found	Calculated
Index of refraction $n_D^{20}$	1.5823	...
Molecular refraction	36.7	36.3
Specific gravity	1.2737	...
Molecular weight	137	136
Sulfur, %	46.3	47.1

Cyclic compounds containing one or more heterocyclic sulfur atoms are well represented in the literature but heterocyclics with a disulfide group are not well known. Fromm and Joerg<sup>6</sup> reported on the ring



which they obtained by the reaction of  $\text{ClC}_2\text{H}_4\text{SSC}_2\text{H}_4\text{Cl}$  with  $\text{Na}_2\text{S}$  or  $\text{ClC}_2\text{H}_4\text{SC}_2\text{H}_4\text{Cl}$  with  $\text{Na}_2\text{S}_2$ . They reported a melting point of 74 to 75° for the product obtained by either method.

The production of polymer would appear more probable from this method of preparation than would the formation of a cyclic monomer. By substantially the same procedure, we have prepared polymeric products.

Cyclic compounds similar to that resulting from the ether disulfide have been obtained from disulfide polymers of different structures, but the products have yet to be characterized. A complete account of this work, together with theoretical considerations, will appear at a later date.

COMMUNICATION FROM  
THE THIOROL CORPORATION  
TRENTON, N. J.

F. O. DAVIS  
E. M. FETTES

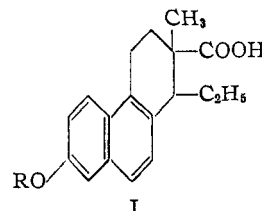
RECEIVED APRIL 20, 1948

(5) J. C. Patrick, *Trans. Faraday Soc.*, **32**, 347 (1946).  
(6) Fromm and Joerg, *Ber.*, **58**, 304 (1925).

## BIS-DEHYDRODOISYNOLIC ACID

Sir:

The substance I ( $\text{R} = \text{H}$ ) has recently attracted considerable attention because it is one of the most potent estrogens known. In a series of brilliant studies Miescher, Heer and Billeter obtained I ( $\text{R} = \text{H}$ ) both as a degradation product



of natural equilenin and by total synthesis.<sup>1</sup> More recently Anner and Miescher<sup>2</sup> announced an improved synthesis involving about ten steps from 1-aminonaphthalene-6-sulfonic acid (Cleve's acid) to the methyl ether I ( $\text{R} = \text{CH}_3$ ). We wish to disclose herewith a facile total synthesis of this substance utilizing the Stobbe condensation of diethyl succinate with 2-propionyl-6-methoxynaphthalene (readily available by Friedel-Crafts acylation of  $\beta$ -naphthyl methyl ether<sup>3</sup>). Catalytic hydrogenation of the resulting condensation product over platinum oxide gave  $\beta$ -carboxy- $\gamma$ -(6-methoxy-2-naphthyl)-caproic acid (m. p. 157–158°, dec. *Anal.* Calcd. for  $\text{C}_{18}\text{H}_{20}\text{O}_6$ : C, 68.34; H, 6.37. Found: C, 68.30; H, 6.30) which on cyclization *via* the anhydride with aluminum chloride in nitrobenzene produced 1-ethyl-4-keto-7-methoxy-1,2,3,4-tetrahydrophenanthrene-2-carboxylic acid, m. p. 215.5–216.5° (*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{18}\text{O}_4$ : C, 72.47; H, 6.08. Found: C, 72.31; H, 6.03). Hydrogenation of the keto acid over palladium-on-charcoal catalyst in the presence of a trace of perchloric acid gave 1-ethyl-7-methoxy-1,2,3,4-tetrahydrophenanthrene-2-carboxylic acid, m. p. 203.5–206°. (*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{20}\text{O}_3$ : C, 76.03; H, 7.09. Found: C, 76.36; H, 7.07), which on treatment in ether solution with diazomethane followed by sodium triphenylmethyl and methyl iodide afforded upon hydrolysis normal bis-dehydrodoisynolic acid methyl ether I ( $\text{R} = \text{CH}_3$ ), m. p. 230–231° alone or when mixed with an authentic specimen of the same melting point which was kindly supplied by Dr. C. R. Scholz of Ciba Pharmaceutical Products. The methyl ester of I ( $\text{R} = \text{CH}_3$ ) melted at 74.5–76.5° and gave no melting point depression on admixture with the ester (m. p. 75–76.5°) prepared from authentic I ( $\text{R} = \text{CH}_3$ ).

Bioassays kindly performed by Drs. R. K. Meyer and E. G. Shipley of the University of Wisconsin Zoology Department showed our acid

(1) Miescher, *Helv. Chim. Acta*, **27**, 1727 (1944); Heer, Billeter and Miescher, *ibid.*, **28**, 991, 1342 (1945).  
(2) Anner and Miescher, *Helv. Chim. Acta*, **29**, 586 (1946).  
(3) Haworth and Sheldrick, *J. Chem. Soc.*, 864 (1934).

to be of the same order of activity as the authentic material.

LABORATORY OF ORGANIC CHEMISTRY

UNIVERSITY OF WISCONSIN  
MADISON, WISCONSIN

WILLIAM S. JOHNSON  
ROBERT P. GRABER

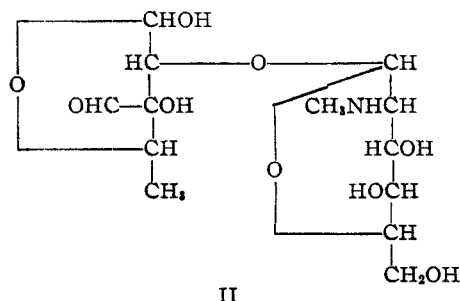
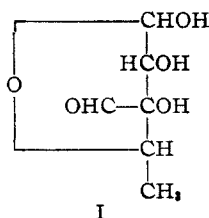
RECEIVED JUNE 14, 1948

**STREPTOMYCES ANTIBIOTICS. XIX. DIHYDRO-STREPTOSONIC ACID LACTONE AND CONFIGURATION OF STREPTOSE AND STREPTOBIOSSAMINE**

Sir:

2-Methyl pentaacetyldihydrostreptobiosamide<sup>1</sup> was allowed to react stepwise with ethyl mercaptan-hydrogen chloride, acetic anhydride, and mercuric chloride for the preparation of amorphous pentaacetyldihydrostreptobiosamine.<sup>2</sup> Acetylation of this compound gave hexaacetyldihydrostreptobiosamine.<sup>2</sup> Oxidation by bromine and hydrolysis by hydrochloric acid of pentaacetyldihydrostreptobiosamine gave the known N-methyl-L-glucosamine and the new dihydrostreptosonic acid lactone, m. p. 143–144°,  $[\alpha]_D -32^\circ$  (c, 0.40 in water). Reaction of the lactone with hydrazine gave dihydrostreptosonic acid hydrazide, m. p. 137–139°,  $[\alpha]_D +23^\circ$  (c, 0.9 in water).

Application of Hudson's rules of rotation to streptosonic acid diamide<sup>3</sup> and dihydrostreptosonic acid hydrazide shows that the hydroxyl group at C<sub>2</sub> of streptose lies on the right. Since it has already been shown<sup>4</sup> that the hydroxyl groups at C<sub>2</sub> and C<sub>3</sub> of streptose are *cis*, and that the configuration about C<sub>4</sub> is *levo*,<sup>5</sup> the configuration of L-streptose is represented by structure I. On the basis of these data, and the calculations of the glycosidic linkage between streptose and N-



(1) Brink, Kuehl, Flynn and Folkers, *THIS JOURNAL*, **68**, 2557 (1946).

(2) Staveland, Wintersteiner, Fried, White and Moore, *ibid.*, **69**, 2742 (1947).

(3) Kuehl, Flynn, Brink and Folkers, *ibid.*, **68**, 2679 (1946).

(4) Brink, Kuehl, Flynn and Folkers, *ibid.*, **68**, 2405 (1946).

(5) Fried, Walz, and Wintersteiner, *ibid.*, **68**, 2746 (1946).

methyl-L-glucosamine to be  $\alpha$ -L,<sup>6</sup> the configuration of streptobiosamine is represented by structure II. The levorotations of streptosonic acid lactone<sup>3</sup> and dihydrostreptosonic acid lactone support the applicability of Hudson's rules to these streptose derivatives, since it is established conclusively that the configuration about C<sub>4</sub> of these lactones is L. That the lactone of dihydrostreptosonic acid lactone involves the secondary hydroxyl group at C<sub>4</sub> is shown by the liberation of formaldehyde when the lactone reacts with two equivalents of periodic acid.

(6) Lemieux, DeWalt and Wolfrom, *ibid.*, **69**, 1838 (1947).

RESEARCH DEPARTMENT  
MERCK AND CO., INC.  
RAHWAY, N. J.

FREDERICK A. KUEHL, JR.  
MARY NEALE BISHOP  
EDWIN H. FLYNN  
KARL FOLKERS

RECEIVED MAY 27, 1948

**CHARACTERISTICS OF THE DROPPING MERCURY ELECTRODE IN FUSED SALTS**

Sir:

In a preliminary investigation of the applicability of polarographic techniques to fused salt media we have obtained typical polarographic reduction waves for the cations of a number of salts dissolved in a fused salt solvent. The results indicate that the Ilkovic equation<sup>1,2</sup> is applicable to the melt employed, a ternary eutectic consisting of 66.65 mole % ammonium nitrate, 25.76% lithium nitrate, and 7.59% ammonium chloride (m. p. 86.2°).<sup>3</sup>

Mercury was used for the dropping electrode and the stationary unpolarized anode pool in a cell maintained at  $125 \pm 0.5^\circ$  in an oil-bath. Drops were collected in a Pyrex spoon, washed, dried, and weighed for tests of the Ilkovic equation.

Characteristic reduction waves were obtained with nickel(II), copper(II), and bismuth(III), the latter two exhibiting maxima. A trace of potassium iodide eliminated the maximum in the case of copper. Varying degrees of success have been had with other solute salts, prime difficulties being limited solubility in or reaction with the solvent electrolyte.

TABLE I  
TEST OF THE ILKOVIC EQUATION

No.	C, mmol./l.	$i_d$ , $\mu$ amp.	$m$ , mg./sec.	$i_{\max.}$ , sec.	$\frac{i_d}{Cm^{3/4}t^{1/4}}$ $\frac{i_{\max.}}{Cm^{3/4}t^{1/4}}$
1	1.95	3.74	1.41	4.0	1.21
2	4.98	10.0	1.45	4.5	1.22
3	6.77	12.8	1.37	3.9	1.22
4	9.97	17.2	1.45	3.4	1.10
5	12.8	21.6	1.40	3.5	1.09
6	12.8	16.6	0.658	7.6	1.22

(1) D. Ilkovic, *Coll. Czechoslov. Chem. Commun.*, **8**, 498 (1934).

(2) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 88.

(3) E. P. Perman and R. H. Wilson, *J. Chem. Soc.*, **125**, 1700 (1924).