C, 12.2; H, 0.23; B, 14.6; Br, 27.0; Cs, 29.9; N, 14.2. Found: C, 12.2; H, 0.40; B, 14.2; Br, 26.5; Cs, 29.6; N, 14.2); the B^{11} n.m.r. spectrum[3] which shows only two peaks at $+27.5$ and $+33.0$ p.p.m. with relative areas of 3:9; and the infrared spectrum which shows nitrile absorption at 2200 cm.$^{-1}$ and is otherwise simple with strong bands at 1142, 1115, 980, 950, and 920 cm.$^{-1}$. The species $B_{12}Cl_5$-$(CN)_7^{2-}$ was obtained in analogous fashion from B_{12}-Cl_{12}^{2-}. *Anal.* Calcd. for $Cs_2B_{12}C_7Cl_5N_7$: C, 11.1; B, 17.2; Cl, 23.5; N, 13.0. Found: C, 11.1; B, 17.3; Cl, 24.1; N, 12.8.

By contrast, $B_{10}Cl_{10}^{2-}$ was much less reactive and under comparable conditions yielded a mixture of B_{10}-Cl_9CN^{2-}, $B_{10}Cl_8(CN)_2^{2-}$, and $B_{10}Cl_7(CN)_3^{2-}$ from which the first two species were isolated. *Anal.* Calcd. for $CCs_2B_{10}Cl_9N$: C, 1.67; B, 15.0; Cl, 44.3; N, 1.94. Found: C, 2.04; B, 14.9; Cl, 44.3; N, 1.65. Calcd. for the tetramethylammonium salt of $B_{10}Cl_8$-$(CN)_2^{2-}$, $C_{10}H_{24}B_{10}Cl_{10}N_4$: C, 20.4; H, 4.06; B, 18.3; Cl, 48.0; N, 9.47. Found: C, 20.3; H, 4.38; B, 18.1; Cl, 47.8; N, 8.66. While the stereochemistry of the $B_{10}Cl_8(CN)_2^{2-}$ compound was not established, its infrared spectrum was strikingly different from that of $B_{10}Cl_8(CN)_2^{2-}$ prepared by exhaustive chlorination of $B_{10}H_8(CN)_2^{2-}$ containing 1,10-cyano groups.[4] The reactivity seems thus to be the inverse of that observed in the case of electrophilic substitution.

The reaction is thought to proceed through a photo-induced heterolysis of the boron–halogen bond resulting in an electron-deficient species. This reacts with a suitable base to regenerate the dianion bearing at this point a new substituent, *viz.*

$$B_{12}X_{12}^{2-} \xrightarrow{h\nu} B_{12}X_{11}^- + X^- \xrightarrow{Z^-} B_{12}X_{11}Z^{2-}$$
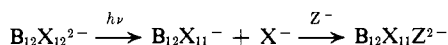
The above scheme is in accord with the finding that when $B_{12}Br_{12}^{2-}$ is irradiated in the presence of chloride ion or $B_{12}Cl_{12}^{2-}$ in the presence of bromide ion, halogen exchange takes place, the former being seven times faster than the latter. This is in line with bromine being (1) a better departing ion and (2) a better stabilizer of the electron-deficient intermediate through forms such as $(B_{12}Br_{10} \doteq {}^{2-}Br^+$. Furthermore, irradiation of $B_{12}Br_{12}^{2-}$ in the presence of N_3^-, OCN^-, and other anions has yielded appropriately substituted derivatives.

The details of this work will be described in a forthcoming publication.

(3) The B^{11} n.m.r. spectrum was determined at 19.25 Mc. and the chemical shifts are referred to external methyl borate.
(4) W. H. Knoth, J. C. Sauer, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 115 (1964).

S. Trofimenko, H. N. Cripps

Contribution No. 1024, Central Research Department
Experimental Station, E. I. du Pont de Nemours and Co.
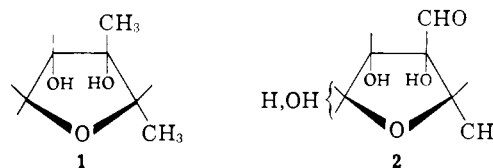*Wilmington 98, Delaware*
Received November 5, 1964

Streptomycin. II.[1] Streptose

Sir:

A unique feature in the determination of the structure of the potent antibacterial substance streptomycin is that the central carbohydrate fragment, streptose,

(1) J. R. Dyer and A. W. Todd, *J. Am. Chem. Soc.*, **85**, 3896 (1963), is regarded as paper I of this series.
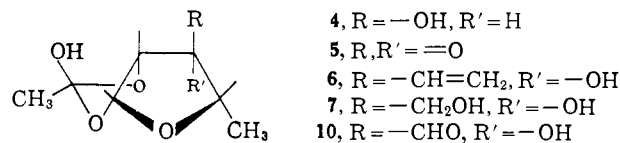
has never been isolated as a degradation product. Through studies of the chemistry and properties of various derivatives and transformation products of streptose, its structure was established[2] in 1946 to be a 2,3,4-trihydroxy-3-C-formylvaleraldehyde. The absolute stereochemistry of streptose was established to be (R) (L) at C-4[3] and (S) (D) at C-2.[4] Because dideoxy-dihydrostreptose (1) enhanced the acidity of boric acid solutions,[5] the hydroxyl groups at C-2 and C-3 of 1 were presumed to be *cis* oriented and the configurations at C-2 and C-3 of streptose were presumed to be similar. Consequently, streptose was assigned the structure 3-C-formyl-5-deoxy-L-lyxofuranose (2). We report total syntheses of streptose and several deriva-

tives and transformation products of streptose that fully substantiate the assigned structures.

Potassium permanganate hydroxylation of 2,3-dimethyl-2,5-dihydrofuran[6] gave a 50% yield of a mixture of *cis*-diols, whose composition (g.l.c.) was approximately 1:2[7] *dl*-dideoxydihydrostreptose (1)[9] and an isomer (3). Synthetic *dl*-dideoxydihydrostreptose, m.p. 62.0–62.2°, had infrared and n.m.r. spectra identical with those of a naturally derived sample[10] (1) and identical g.l.c. behavior. The *dl* isomer 3, m.p. 58.5–59.5°, had markedly different infrared and n.m.r. spectra and different g.l.c. behavior.

Oxidation of 1,2-O-isopropylidene-5-deoxy-β-L-arabinofuranose[11] (4), using dicyclohexylcarbodiimide, pyri-

dinium phosphate, and dimethyl sulfoxide,[12] gave sirupy 1,2-O-isopropylidene-5-deoxy-β-L-*threo*-pentofuranos-3-ulose (5), $[\alpha]D$ $+76°$, characterized as a crystalline oxime, m.p. 104–105.5°, $[\alpha]D$ $-10°$. Reaction of the ketone 5 with vinylmagnesium bromide gave 1,2-O-isopropylidene-3-C-vinyl-5-deoxy-β-L-lyxofuranose (6),[13] m.p. 67.5–68.5°, $[\alpha]D$ $+21°$. Ozonol-

(2) R. U. Lemieux and M. L. Wolfrom, *Advan. Carbohydrate Chem.*, **3**, 337 (1948), and references cited therein.
(3) J. Fried, D. E. Walz, and O. Wintersteiner, *J. Am. Chem. Soc.*, **68**, 2746 (1946).
(4) M. L. Wolfrom and C. W. DeWalt, *ibid.*, **70**, 3148 (1948).
(5) N. G. Brink, F. A. Kuehl, Jr., E. H. Flynn, and K. Folkers, *ibid.*, **68**, 2405 (1946).
(6) E. E. Schweizer, *ibid.*, **86**, 2744 (1964).
(7) This is to be anticipated since *cis* hydroxylations of olefins by potassium permanganate are known to proceed predominantly from the less sterically hindered side.[8]
(8) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 358.
(9) Satisfactory analytical results were obtained for all new compounds reported.
(10) We are grateful to Mr. R. K. Chawla for the preparation of an authentic sample of this substance.
(11) P. A. Levene and J. Compton, *J. Biol. Chem.*, **116**, 189 (1936).
(12) K. E. Pfitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, **85**, 3027 (1963).
(13) If the Grignard reagent adds to the less sterically hindered side of 5, as would be anticipated,[14] the desired *lyxo*, rather than *arabino*, configuration results. G.l.c. analysis of the crude product failed to reveal any other component with a retention time comparable to that of 6.
(14) Ref. 9, p. 69.

ysis of **6**, followed by direct reduction with sodium borohydride, gave 1,2-O-isopropylidene-3-C-hydroxy-methyl-5-deoxy-β-L-lyxofuranose (**7**), m.p. 104–106°, [α]D +7.6°. Deacetonation of **7** was accomplished by stirring an aqueous solution of **7** with Dowex-50 (H⁺) at room temperature for 2 days. This produced, after chromatography over carbon, L-dihydrostreptose (**8**),[15,18] a sirupy mixture of anomeric C-4[19] furanoses, [α]D −24°, whose n.m.r. spectrum in deuterium oxide showed absorptions of two isomers. The β[20] anomer comprised 74% of the mixture and showed absorptions at τ 8.76 (3 H, doublet, J = 6.6 c.p.s.), 6.38 (2 H, singlet), 5.85 (1 H, doublet, J = 3.8 c.p.s.), 5.65 (1 H, quartet, J = 6.6 c.p.s.), and 4.72 (1 H, doublet, J = 3.8 c.p.s.). The α anomer showed absorptions at τ 8.71 (3 H, doublet, J = 6.6 c.p.s.), 6.38 (2 H, singlet), 5.91 (1 H, quartet, J = 6.6 c.p.s.), 5.82 (1 H, doublet, J = 5.1 c.p.s.), and 4.76 (1 H, doublet, J = 5.1 c.p.s.). The yield of dihydrostreptose from **4** was 23%. Synthetic dihydrostreptose gave, in poor yield, a tosylhydrazone, m.p. 133–137° (lit.[16] m.p. 137.5–138°). Bromine water oxidation converted synthetic dihydrostreptose, in 60% yield, to dihydrostreptosonic acid lactone (**9**), m.p. 140.5–142.5°, [α]D −32° (lit.[22] m.p. 143–144°, [α]D −32°). Synthetic **9** showed the expected infrared[22] and n.m.r. absorptions.

8

9, R = —CH₂OH
11, R = —CO₂H
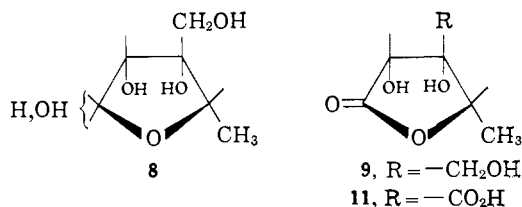
Catalytic hydrogenation of the ozonide of **6** gave 1,2-O-isopropylidene-3-C-formyl-5-deoxy-β-L-lyxofuranose (**10**) which, on reduction with sodium borohydride, gave **7** in 55% yield. Deacetonation of **10** by stirring with water–dioxane and Dowex-50 (H⁺) at room temperature for 2 days furnished, after chromatography on carbon, L-streptose (**2**),[18] [α]D −18°, a glass. The n.m.r. spectrum of streptose in deuterium oxide showed absorptions assigned to two

(15) Wang and co-workers[15] obtained, by partial reduction of naturally derived dihydrostreptosonic acid lactone, a mixture of substances, one of which was claimed to be dihydrostreptose. The sirupy dihydrostreptose obtained (no rotation given) was characterized by a crystalline tosylhydrazone, m.p. 137.5–138°. McGilveray and Stenlake[17] have recently claimed the isolation of dihydrostreptose by mild acid hydrolysis of methyl N-acetyldihydrostreptobiosaminide (m.p. 140°, [α]D − 125°). They reported that their product was a hygroscopic solid that had m.p. 135–140° and [α]D − 70°; the product was characterized as a *mono*acetyl derivative, m.p. 173°. We suggest that this preparation was composed of some dihydrostreptose (or some decomposition product of dihydrostreptose) and the starting material. The constitution of the acetyl derivative reported is obscure.

(16) Y. Wang, H.-Y. Loh, W.-T. Lin, and C.-H. Chang, *Acta chim. Sinica*, **25**, 257 (1959).

(17) I. J. McGilveray and J. B. Stenlake, *Chem. Ind.* (London), 238 (1964).

(18) Dihydrostreptose and streptose were each chromatographically homogeneous.

(19) That no significant amount of C_branch furanose isomer was present is shown by the fact that the C_branch methylene group protons absorb (n.m.r.) at τ 6.38, the same value as the corresponding protons in **7** and **9**.

(20) The anomer present in larger amount is tentatively assigned the β configuration. Detailed examination of the n.m.r. spectra of these and related compounds and optical activity calculations using the method of Brewster[21] support this assignment.

(21) J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5483 (1959).

(22) F. A. Kuehl, Jr., R. L. Clark, M. N. Bishop, E. H. Flynn, and K. Folkers, *ibid.*, **71**, 1445 (1949).

anomeric C-4 furanose aldehyde hydrates corresponding to structure **2**. The β[20] anomer, which comprised 79% of the mixture, showed absorptions at τ 8.73 (3 H, doublet, J = 6.5 c.p.s.), 5.81 (1 H, doublet, J = 4.1 c.p.s.), 5.55 (1 H, quartet, J = 6.5 c.p.s.), 4.97 (1 H, singlet), and 4.77 (1 H, doublet, J = 4.1 c.p.s.). The α anomer showed absorptions at τ 8.68 (3 H, doublet, J = 6.6 c.p.s.), 5.75 (1 H, quartet, J = 6.6 c.p.s.), 5.64 (1 H, doublet, J = 5.1 c.p.s.), 4.97 (1 H, singlet), and 4.73 (1 H, doublet, J = 5.1 c.p.s.). The over-all yield of streptose from **4** was 36%. Synthetic streptose, when oxidized by bromine water, gave streptosonic acid monolactone (**11**), m.p. 154–156°, [α]D −41° (lit.[23] m.p. 146–148°, [α]D −37°)[24] in 50% yield. The infrared (KBr pellets) and n.m.r. spectra of synthetic and authentic[10] streptosonic acid monolactone (**11**) were identical.

Because N-methyl-L-glucosamine[25] and streptidine[26] have been synthesized and the asymmetry of the streptidine ring carbons has been established,[1] the results reported complete the synthetic proof of the structure of streptomycin and the stereochemistry assigned to all the asymmetric centers except the glycosidic linkages.

(23) F. A. Kuehl, Jr., E. H. Flynn, N. G. Brink, and K. Folkers, *ibid.*, **68**, 2679 (1946).

(24) Our authentic sample[10] of streptosonic acid monolactone showed m.p. 154.5–156.6° and [α]D − 41°. The mixture melting point of authentic and synthetic samples was 153.5–155.5°.

(25) F. A. Kuehl, Jr., E. H. Flynn, F. W. Holly, R. Mozingo, and K. Folkers, *J. Am. Chem. Soc.*, **69**, 3032 (1947).

(26) M. L. Wolfrom, S. M. Olin, and W. J. Polglase, *ibid.*, **72**, 1724 (1950).

(27) National Institutes of Health Predoctoral Fellow, 1962–1964.

John R. Dyer, W. E. McGonigal,[27] **K. C. Rice**
School of Chemistry,
Georgia Institute of Technology
Atlanta, Georgia 30332

A Stable Dianion of Naphthalene

Sir:

Aromatic hydrocarbons react with alkali metals in suitable solvents, such as tetrahydrofuran, forming mono- or dinegative ions.[1,2] The mononegative radical-ions proved to be paramagnetic, since they possess an extra electron in the lowest unoccupied π-orbital,[3] whereas the dinegative ions, *e.g.*, anthracene⁻²2Na⁺, are diamagnetic and may be represented as species possessing two coupled electrons in that orbital. The driving force leading to the formation of such ions is determined by the electron affinity of the parent aromatic hydrocarbon and by the solvation of the resulting ions or ion pairs. The total free energy of their formation is measured by the reduction potential of the respective hydrocarbon,[4,5] which is usually larger for the first step (formation of the mononegative ions) than

(1) W. Schlenk and E. Bergmann, *Ann.*, **463**, 1 (1928).

(2) N. D. Scott, J. F. Walker, and V. L. Hansley, *J. Am. Chem. Soc.*, **58**, 2442 (1936).

(3) D. E. Paul, D. Lipkin, and S. I. Weissman, *ibid.*, **78**, 116 (1956).

(4) J. Hoijtink, E. de Boer, P. H. van der Meij, and W.P. Weyland, *Rec. trav. chim.*, **75**, 487 (1956).

(5) J. Jagur-Grodzinski, M. Feld, S. L. Yang, and M. Szwarc, *J. Phys. Chem.*, in press.