

to obtain evidence as to whether a single intermediate is involved (which returns with partial loss of configuration) or if two intermediates are involved<sup>13</sup> (one which returns with preservation of configuration and the other with partial or complete loss of configuration).

We also have examined the solvolysis product, *p*-chlorobenzhydrol. For solvolysis in 80% acetone the alcohol is 8% as optically pure (retention of configuration) as the average optical purity<sup>14</sup> of the ester from which it was derived. This means that solvolysis proceeds with 92% loss of configuration and 8% retention of configuration. Solvolysis in 90% acetone proceeds with 10% retention of configuration. In this connection it is significant that control experiments demonstrated that (a) solvolysis involves at least 99% alkyl-oxygen cleavage and (b) the alcohol does not undergo any change (racemization or oxygen exchange) under the conditions of the solvolysis. The partial retention suggests that the present solvolysis is related to the microscopic reverse of the cleavage of  $\alpha$ -phenylethyl aryl ethers with hydrogen chloride reported by Hart and co-workers.<sup>15</sup>

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(13) See S. Winstein, P. E. Klinedinst, Jr., and E. Clippinger, *J. Am. Chem. Soc.*, **83**, 4986 (1961).

(14) Determined as described by S. Winstein and D. Trifan, *ibid.*, **74**, 1154 (1952).

(15) H. Hart and R. J. Elia, *ibid.*, **83**, 985 (1961); H. Hart and H. S. Eleuterio, *ibid.*, **76**, 1379 (1954). See also K. Okamoto, K. Takeuchi, and H. Shingu, *Bull. Chem. Soc. Japan*, **35**, 525 (1962).

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### The Identification and Synthesis of the 4-Aminosugar from *Chromobacterium violaceum*

Sir:

We wish to report the complete identification and synthesis of viosamine, 4,6-dideoxy-4-amino-D-glucose, isolated from the lipo-polysaccharide of *C. violaceum*, NCTC 7917.<sup>1</sup> This 4-aminosugar represents the first of a new class of carbohydrates isolated and identified from the special polysaccharides of bacteria.

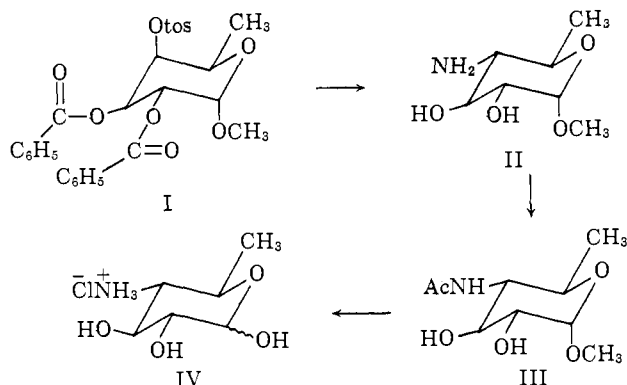
Further, we suggest that this class of carbohydrate may be of wide occurrence and importance, since, in addition to its presence in the lipopolysaccharide of *C. violaceum*, the N,N-dimethyl derivative has been shown to occur in the antibiotic amicetin, and since the properties of viosamine indicate that it is identical with one of the new aminosugars isolated by Strominger<sup>2</sup> as a thymidine diphosphate nucleotide conjugate (TDP-X<sub>2</sub>) from *Escherichia coli* B.

(1) R. W. Wheat, E. L. Rollins, and J. M. Leatherwood, *Biochem. Biophys. Res. Commun.*, **9**, 120 (1962).

(2) T. Okazaki, R. Okazaki, J. L. Strominger, and S. Suzuki, *ibid.*, **7**, 300 (1962). A private communication from J. L. Strominger indicates N-acetyl viosamine appears to be identical with X<sub>2</sub> by paper chromatography in the three solvents reported in his article and by comparison of infrared spectra and that viosamine is identical with deacylated X<sub>2</sub> in the three solvent systems of ref. 1.

Natural crystalline viosamine hydrochloride was isolated as previously described,<sup>1</sup> m.p. 132–138° dec.,  $[\alpha]^{25}_D -9^\circ$  initial  $\rightarrow +21^\circ$  (24 hr., *c* 1, H<sub>2</sub>O).

Synthetic viosamine hydrochloride was prepared starting with methyl-6-deoxy-4-tosyl- $\alpha$ -D-galactopyranoside dibenzoate<sup>3</sup> (I), m.p. 157–158°. Treatment with azide ion<sup>4</sup> followed by reduction with platinum catalyst and saponification with barium hydroxide gave methyl-4,6-dideoxy-4-amino- $\alpha$ -D-glucopyranoside (II), m.p. 117–118°;  $[\alpha]^{25}_D +144^\circ$  (*c* 0.85, H<sub>2</sub>O). The crystalline N-acetate III was prepared, m.p. 188–189.5°;  $[\alpha]^{25}_D +151^\circ$  (*c* 0.43, H<sub>2</sub>O). The free amine I and the N-acetate III were subjected to periodate studies to confirm their structure; II consumed 2 moles of periodate at a rate essentially identical with that of methyl- $\alpha$ -D-glucopyranoside. The N-acetate III consumed one mole of periodate at a much slower rate.



Many attempts to hydrolyze the  $\alpha$ -methyl glycoside II failed to give a crystalline product, as did the many attempts to convert the natural viosamine into its  $\alpha$ -methyl glycoside. Hydrolysis of the  $\alpha$ -methyl glycoside N-acetate III was successful, using 2.5 *N* hydrochloric acid for 6.5 hr. at 100°. Crystalline synthetic viosamine hydrochloride (IV) was isolated in 58% yield after cation exchange chromatography, m.p. 130–138° dec.,  $[\alpha]^{25}_D -12^\circ$ , 8 min.  $\rightarrow +20^\circ$  (22 hr., *c* 0.76, H<sub>2</sub>O). The decomposition point and optical rotation data correspond with the natural material. The infrared spectra of the natural and synthetic material were superimposable and the *R<sub>f</sub>* values were identical in three systems: 1-butanol-acetic acid-water (5:1:2), *R<sub>f</sub>* 0.14; phenol-water (3:1), *R<sub>f</sub>* 0.27; and 1-butanol-ethanol-water-ammonium hydroxide (5:1.4:3:0.1), *R<sub>f</sub>* 0.44.

The n.m.r. spectrum of the free aminosugar hydrochloride in deuterium oxide supported the gluco-configuration.

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(3) C. L. Stevens, P. Blumbergs, and F. A. Daniher, *J. Am. Chem. Soc.*, **85**, 1552 (1963).

(4) Cf. E. J. Reist, R. R. Spencer, B. R. Baker, and L. Goodman, *Chem. Ind. (London)*, 1794 (1962), who show that a 4-mesyl group in the galactose series is displaced with inversion by azide ion in dimethylformamide solvent.

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