

From molecular weight determinations using benzene solutions, Hill¹⁵ concluded that at higher concentrations, two or even three ion pairs of silver perchlorate associated into clusters. Estimations of the size of the solute particle by Luder, *et al.*,²¹ also indicate dimerization. It may prove possible to determine the solute particle geometry by an

(21) W. L. Luder, P. B. Kraus, C. A. Kraus and R. M. Fuoss, *THIS JOURNAL*, **58**, 255 (1936).

X-ray diffraction technique, using concentrated solutions of silver perchlorate or fluoborate in toluene, such as was carried out by Vaughan, *et al.*,²² with complex ions of certain heavy metals.

(22) P. A. Vaughan, J. H. Sturdivant and L. Pauling, *ibid.*, **72**, 5477 (1950).

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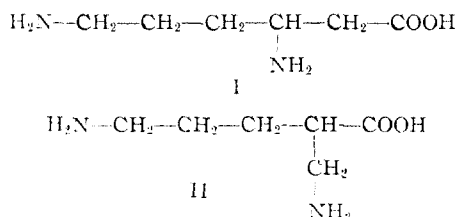
COMMUNICATIONS TO THE EDITOR

STRUCTURE OF THE DIAMINOHEXANOIC ACID FROM STREPTOTHRICIN¹

Sir:

Previously we have reported that streptothricin on hydrolysis yields three ninhydrin-positive products, one of which, the fastest-moving on papergrams, was characterized as a diamino hexanoic acid.^{2,3} The same amino acid has been isolated from viomycin^{3,4,5} and appears to be present also in streptolin.^{3,6}

Possible structures for this substance were limited to isomers I and II on the basis of the following data^{2,3}: negative Kuhn-Roth, negative



periodate, and negative α -amino acid tests; degradation *via* the Curtius reaction to a triamino-pentane which reacted with periodate (one mole) yielding ammonia and formaldehyde.

Since further degradation studies were unproductive, the synthesis of isomers I and II was undertaken. I was obtained from α -N-phthalyl- δ -N-benzoyl-L-ornithine by application of the Arndt-Eistert reaction in a manner similar to that described by Balenović, *et al.*,⁷ for derivatives of tyrosine. The resulting β, ϵ -diamino-*n*-caproic acid

(1) Supported by a grant from the Abbott Laboratories, Eli Lilly and Company, and the Upjohn Company.

(2) H. E. Carter, W. R. Hearn and W. R. Taylor, "Abstracts of Papers," 119th Meeting, American Chemical Society, Cleveland, Ohio, April, 1951, p. 25A.

(3) H. E. Carter, W. R. Hearn and W. R. Taylor, "Abstracts of Papers," 120th Meeting, American Chemical Society, New York, N. Y., September, 1951, p. 3L.

(4) T. H. Haskell, S. A. Fusari, R. P. Frohardt and Q. R. Bartz, *THIS JOURNAL*, **74**, 599 (1952).

(5) We are indebted to Parke, Davis and Company for a generous supply of viomycin.

(6) E. E. Smisson, R. W. Sharpe and E. E. van Tamelen, "Abstracts of Papers," 121st Meeting, American Chemical Society, Milwaukee, Wisconsin, April, 1952, p. 80.

(7) von K. Balenović, V. Thaller and I. Pilipović, *Helv. Chim. Acta*, **34**, 744 (1951).

was optically active ($[\alpha]^{25D} +24^\circ$, c 1.1 in 1 *N* hydrochloric acid), and yielded the following derivatives: *p*-hydroxyazobenzene-*p'*-sulfonate, m.p. 246–249°; *N,N*-dibenzoyl acid, m.p. 113–116° (found: C, 67.94; H, 6.30; N, 7.73); *N,N*-dibenzoyl methyl ester, m.p. 147–150° (found: C, 68.47; H, 6.42; N, 7.77). The corresponding derivatives of the natural substance ($[\alpha]^{25D} +25^\circ$, c 1.1 in 1 *N* hydrochloric acid) melted at 224–246° (found: C, 51.52; H, 4.44; N, 12.23; S, 9.30), 113–116° (found: C, 68.02; H, 5.73; N, 7.93), and 148–150° (found: C, 68.63; H, 6.22; N, 7.86), respectively. The infrared spectra of the *N,N*-dibenzoyl acids and esters of the synthetic and natural substances were respectively identical. Moreover, crystallization from ethanol of the crude benzoylation products of both the synthetic and natural substances yielded neutral dibenzoyl derivatives (synthetic, m.p. 143–146°, found: C, 68.95; H, 6.77; N, 7.43; natural, m.p. 146–148°, found: C, 68.71; H, 6.97; N, 7.89) having superimposable infrared spectra.

Isomer II was prepared in racemic form by reduction of ethyl α, γ -dicyanobutyrate in a glacial acetic-sulfuric acid mixture with platinum oxide as catalyst. The racemic *N,N*-dibenzoyl acid (m.p. 156–158°, found: C, 68.13; H, 5.92; N, 7.66) and *N,N*-dibenzoyl methyl ester (m.p. 119–122°) of II gave infrared spectra differing significantly from those of the corresponding derivatives of the natural substance.

These data establish conclusively that the diamino hexanoic acid from streptothricin and viomycin has structure I (β, ϵ -diamino-*n*-caproic acid). It is suggested that the trivial name β -lysine be assigned to this compound.

Structural studies upon streptothricin and its hydrolytic products will be reported later in more detail.

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