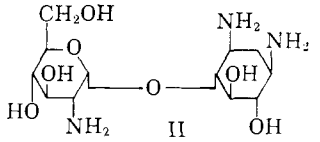
be identical with D-glucosamine hydrochloride by infrared spectrum, X-ray diffraction, optical rotation and comparison of the salicylidene derivatives.

Since the crystalline N,N′,N″-triacetylparomamine [*Anal.* Calcd. for $C_{18}H_{31}N_3O_{10}$ (449.5): C, 48.10; H, 6.95; N, 9.35. Found: C, 48.04; H, 7.03; N, 9.37; $[\alpha]^{25}D$ +108° (*c* 1.0, H_2O); m.p. 300–306° dec.] consumes two moles of periodate[5] with the absence of formaldehyde formation, and paromamine gave negative reduction tests, the structural formula of the latter is represented as II.



II

Since the infrared spectra (KBr) of crystalline paromamine trihydrochloride and paromamine free base show absorption bands at 11.2, 11.91 μ and 11.06, 11.75 μ, respectively, no assignment of anomeric configuration is possible by this method.[6] However, since glucosamine is in the D-series and paromamine trihydrochloride has a high positive molecular rotation (+36,100), an α-D-glycosidic linkage is inferred. Data from methylation experiments described in a subsequent paper have more rigorously established this conclusion.

(5) R. W. Jeanloz and E. Forchielli, *J. Biol. Chem.*, **188**, 361 (1951).
(6) S. A. Barker, E. J. Bourne, M. Stacey and D. H. Whiffen, *J. Chem. Soc.*, 171 (1954); *cf.* "Methods of Biochemical Analysis," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1956, p. 213.

RESEARCH DIVISION
PARKE, DAVIS & COMPANY
DETROIT 32, MICHIGAN

THEODORE H. HASKELL
JAMES C. FRENCH
QUENTIN R. BARTZ

RECEIVED MAY 5, 1959

PAROMOMYCIN. II. PAROMOBIOSAMINE, A DIAMINOHEXOSYL-D-RIBOSE

Sir:

In the previous communication[1] methanolysis of the antibiotic paromomycin was reported to yield paromamine and the α- and β-anomers of methyl paromobiosaminide. This communication deals with preliminary structural studies on the disaccharide moiety, paromobiosamine.

The unresolved anomeric mixture of methyl paromobiosaminides was converted to the amorphous N,N′-dibenzoyl derivative [*Anal.* Calcd. for $C_{11}H_{19}N_2O_7(OCH_3)(COC_6H_5)_2$: C, 58.64; H, 6.06; N, 5.26. Found: C, 58.37; H, 6.25; N, 5.58] melting over a wide range (120–145°). Dilute acid hydrolysis followed by extraction, ion exchange treatment and carbon chromatography afforded a neutral colorless gum which corresponded to ribose in several paper chromatographic systems. Its infrared absorption spectrum in KBr[2] was identical to that of D-ribose. Since it exhibited a negative rotation $[\alpha]^{27}D$ −14° → −18° (18 hr.) the sugar is assigned to the D-series. Reduction with sodium borohydride afforded crystalline ribitol, m.p. 102–103°.

Vigorous acid hydrolysis of methyl paromobiosaminide (6 *N* hydrochloric acid) resulted in complete destruction of the ribose moiety and, following carbon chromatography, afforded an amorphous hygroscopic diaminohexose (paromose) $[\alpha]^{26}D$ +19° (*c* 1.0, H_2O; no mutarotation). Paromose is characterized as its crystalline dipicrate [*Anal.* Calcd. for $C_6H_{14}N_2O_4$ $(C_6H_3N_3O_7)_2$: C, 33.97; H, 3.17; N, 17.61; picric acid, 72. Found: C, 34.15; H, 3.40; N, 17.44; picric acid (via ultraviolet analysis), 70; $[\alpha]^{28}D$ +22° (*c* 0.5, H_2O)] which melted at 126–128° with decomposition. N,N′-Diacetylparomose formed a crystalline *p*-nitrophenylhydrazone (yellow needles) [*Anal.* Calcd. for $C_{16}H_{23}N_5O_7$: C, 48.36; H, 5.83; N, 17.63. Found: C, 48.42; H, 5.82; N, 17.53; $[\alpha]^{28}D$ + 5.9° (*c* 0.4, moist MeOH), m.p. 229–231° dec.]. N-Acetylation of paromose by the method of Roseman and Ludowieg[3] followed by sodium borohydride reduction yielded the crystalline dihydro N,N′-diacetyl derivative [*Anal.* Calcd. for $C_{10}H_{20}N_2O_6$: C, 45.45; H, 7.63; N, 10.60. Found: C, 45.29; H, 7.61; N, 10.50; $[\alpha]^{28}D$ −17.8° (*c* 4.0, 0.2 *M* *p*H 4.5 acetate buffer); m.p. 150.5–151.5°].

Dilute acid hydrolysis (0.5 *N* hydrochloric acid for 5 hours at 92°) of methyl paromobiosaminide produced, in addition to small amounts of starting material and paromose, the reducing disaccharide paromobiosamine which was isolated as the crystalline dihydrochloride [*Anal.* Calcd. for $C_{11}H_{22}N_2O_8 \cdot 2HCl \cdot CH_3OH$ (415.3): C, 34.71; H, 6.80; N, 6.75; Cl, 17.08. Found: C, 34.53; H, 7.13; N, 6.82; Cl, 16.84; neutral equivalent, 204; $[\alpha]^{27}D$ +25.5° (*c* 1.0, H_2O; no mutarotation)] and as the free base having a mutarotation value of +32° (*c* 1.0, H_2O). The ease of methanolysis (0.32 *N* HCl) of paromomycin to methyl paromobiosaminide which in turn can be hydrolysed with 0.5 *N* HCl to the free disaccharide, paromobiosamine, argues strongly in favor of a diaminohexosyl pentose rather than a pentosyl diaminohexose structure. Rinehart and Woo[4] arrive at the same conclusion with the neobiosamines but base their evidence on the detection of ribitol from hydrolysis of N,N′-dibenzoyldihydroneobiosamine C.

(1) T. H. Haskell, J. C. French and Q. R. Bartz, THIS JOURNAL, **81**, 3480 (1959).
(2) F. E. Resnik, L. S. Harrow, J. C. Holmes, M. E. Bill and F. L. Green, *Anal. Chem.*, **29**, 1874 (1957).
(3) S. Roseman and J. Ludowieg, THIS JOURNAL, **76**, 301 (1954).
(4) K. L. Rinehart, Jr., and P. W. K. Woo, *ibid.*, **80**, 6463 (1958).

RESEARCH DIVISION
PARKE, DAVIS & COMPANY
DETROIT 32, MICHIGAN

THEODORE H. HASKELL
JAMES C. FRENCH
QUENTIN R. BARTZ

RECEIVED MAY 5, 1959

PAROMOMYCIN. III. THE STRUCTURE OF PAROMOBIOSAMINE

Sir:

The characterization of paromobiosamine as an *O*-(diaminohexosyl)-D-ribose was described in the previous communication.[1] This report concerns

(1) T. H. Haskell, J. C. French and Q. R. Bartz, THIS JOURNAL, **81**, 3481 (1959).