

give 2.7 g. (66%) of hydrocarbon, m.p. 85–87°. Recrystallization from methanol did not change the m.p. Gas-liquid chromatography (2.7 m. \times 6 mm. column packed with 20 weight % Dow Corning 702 silicone fluid on 40–60 mesh fire brick at 120 ml./min. and 85°) showed this material to be 4 \pm 2% *exo* and 96 \pm 2% *endo*-2-methylbornane.

Anal. Calcd. for C₁₁H₂₀: C, 86.76; H, 13.24. Found: C, 86.56; H, 13.24.

A second preparation of predominantly *endo* racemic 2-methylbornane was effected by heating at reflux for 20 hours a mixture of 42.6 g. of methyl iodide and ethereal bornylmagnesium chloride (from 17.3 g. of *endo*-2-chlorobornane). The solvent was evaporated and the residue, after sublimation, was subjected to preparative gas chromatography (3.6 m. \times 2.2 cm. column packed with 15 weight % Dow Corning High Vacuum grease on 40–60 mesh fire brick at 500 ml./min. and 95°) to give 1.29 g. of bornene, 2.60 g. of bornane and 1.29 g. (8.5%) of mixed 2-methylbornanes, m.p. 91–93.5°, consisting of 81 \pm 2% *endo* and 19 \pm 2% *exo* isomers.

Predominantly *exo*-2-Methylbornane.—A modification of the method of Zeiss and Zwanzig²⁹ was used for the preparation of 2-methylenebornane (1-methyl- α -fenchene). Acetylation of racemic 2-hydroxymethylbornane with acetic anhydride in pyridine gave 2-acetoxymethylbornane, b.p. 111.5–112.5° (7.5 mm.), *n*_D²⁵ 1.4673; reported²⁹ b.p. 90–92° (1.5 mm.), *n*_D²⁵ 1.4672. Pyrolysis of the acetate ac-

(29) H. H. Zeiss and F. R. Zwanzig, *J. Am. Chem. Soc.*, **79**, 1733 (1957).

ording to a general procedure³⁰ (dripping the ester through a Vycor tube containing a packed section 20 cm. long and packed with 5-mm. Pyrex helices at 500–520° in a nitrogen atmosphere) gave 65% (based on recovered acetate) of 2-methylenebornane, m.p. 86–86.5° after two recrystallizations from methanol. Zeiss and Zwanzig²⁸ report m.p. 62.5–64° for partially optically active material. The infrared spectrum of our racemic material was identical with that of the optically active sample prepared by these workers. We are indebted to Dr. H. H. Zeiss for a copy of the infrared spectrum of his material.

Catalytic hydrogenation (platinum oxide, methanol) of 1.16 g. of the above racemic olefin resulted in the absorption of one molar equivalent of hydrogen in 1 hour. The filtered solution was poured into water, the product was extracted with pentane, and the pentane solution, after having been washed with water and dried over calcium sulfate, was filtered, concentrated to a volume of 15 ml., and chromatographed on 70 g. of silica gel. The hydrocarbon was eluted with pentane, the solution concentrated to a small volume, and the remaining pentane was removed in the vacuum line to give 0.77 g. (66%) of white solid, m.p. 101–106°. Two recrystallizations from methanol gave 2-methylbornane, m.p. 107–108°. This material consisted of 29 \pm 2% *endo* and 71 \pm 2% *exo* isomer (by gas chromatography).

Anal. Calcd. for C₁₁H₂₀: C, 86.76; H, 13.24. Found: C, 86.59; H, 13.36.

(30) W. J. Bailey and W. B. Lawson, *ibid.*, **77**, 1606 (1955).

COMMUNICATIONS TO THE EDITOR

A NEW ANHYDRO C₈ SUGAR FROM AN ANTIBIOTIC

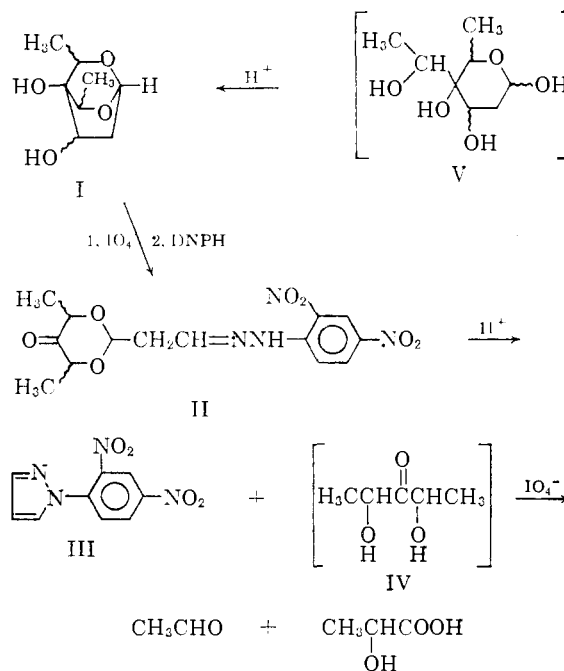
Sir:

We wish to describe studies establishing structure I, Chart A, for a product resulting from mild acid hydrolysis of the *Streptomyces aureofaciens* antibiotic previously designated as " γ -Activity X."¹ It is believed that I has been derived from a branched chain trideoxyoctose, structure V, a representative of a new class of sugars.

The new anhydro sugar was obtained by hydrolyzing a 5% solution of " γ -activity X" in 1 *N* HCl at room temperature for 24 hours. After removal of the insoluble aglycone by filtration, the hydrolysate was adjusted to pH 6.5–7.0 with silver carbonate, clarified, and concentrated under reduced pressure. The syrupy residue was redissolved in water and extracted into ethyl acetate. Evaporation of the combined extracts left an amorphous residue which was taken up in ether, filtered, and concentrated to yield a syrup which partially crystallized on standing. The white crystals were collected, recrystallized from ethyl acetate and found to have the following properties: m.p. 153–154° (with slow sublimation at 120°); [α]_D²⁵ –144° (*c* 2, water). *Anal.* Calcd. for C₈H₁₄O₄ (174): C, 55.16; H, 8.10. Found: C, 55.1; H, 8.1; mol. wt.,² 171. In addition the new com-

(1) J. H. Martin, *et al.*, in H. Welch and F. Marti-Ibáñez, "Antibiotics Annual 1954–1955," Medical Encyclopedia, Inc., New York, N. Y., 1955, pp. 1020–1024.

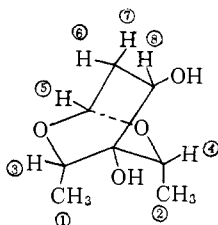
(2) Micro Menzies-Wright method in methanol: D. Ketchum, *Anal. Chem.*, **19**, 504 (1947).



pound was non-reducing, showed neither absorption in the ultraviolet nor carbonyl band in the infrared, gave a positive iodoform test and contained two C-methyl groups by Kuhn-Roth (Calcd. for: 1-CH₃, 8.64; 2-CH₃, 17.3. Found: 10.7,

10.4) and 2.3 active hydrogens, but formed only mono acyl derivatives [mono-3,5-dinitrobenzoate, m.p. 167–168°. *Anal.* Calcd. for $C_{15}H_{16}N_2O_9$ (368): C, 48.91; H, 4.37; N, 7.60. Found: C, 49.1; H, 4.57; N, 7.80].

TABLE I
HIGH RESOLUTION N.M.R. DATA FOR A SATURATED D_2O SOLUTION OF THE $C_8H_{14}O_4$ COMPOUND (I)



Assignment ^a	Chemical shift ^b	Spectrum type	Coupling constants ^c
H ₁ , H ₂	5.26, 5.28 ^e	Two AX ₃	$J_{13} = J_{24} = 6.7$
H ₃ , H ₄	1.94, 2.17 ^e		$J_{67} = 14.9$
H ₅	1.50	X of ABXY	$J_{78} = 3.6$
H ₆	3.97	AB of ABXY	$J_{68} = 9.8$
H ₇	4.63 ^d	($J_{XY} = 0$)	$J_{56} = 2.4$
H ₈	2.18	Y of ABXY	$J_{37} = 1.8$

^a Spectra were recorded at both 40 and 60 Mc. to confirm assignments. ^b Shifts are given in p.p.m. using an external benzene reference. Add 3.51 to convert to approximate τ values. ^c It is not possible to assign separately 1 and 2, or 3 and 4. ^d In assigning H₆ and H₇, H₆ was assumed to be the proton with the larger coupling to H₈ (near-zero dihedral angle). ^e J values are the absolute values, read from the first-order splittings, in c.p.s.

Structure I for the $C_8H_{14}O_4$ sugar followed from the transformations shown in Chart A. Reaction with one mole of periodate was rapid, without fragmentation and produced a dicarbonyl compound isolated³ as a mono-2,4-dinitrophenylhydrazone (II) [m.p. 128–130°. *Anal.* Calcd. for $C_{14}H_{16}N_4O_7$: C, 47.77; H, 4.57; N, 15.9. Found: C, 47.8; H, 4.93; N, 16.2] and also as a bis-2,4-dinitrophenylhydrazone [m.p. 185–190°. *Anal.* Calcd. for $C_{20}H_{20}N_8O_{10}$ (532): C, 45.11; H, 3.78; N, 21.05. Found: C, 45.2; H, 4.10; N, 20.9]. Acid hydrolysis of II formed 1-(2,4-dinitrophenyl)pyrazole (III) [m.p. 107–108°, $\lambda_{\text{max}}^{\text{CH}_2\text{OH}}$ 303 m μ ($\epsilon = 11,700$). *Anal.* Calcd. for $C_9H_8N_4O_4$ (234): C, 46.2; H, 2.56; N, 23.9. Found: C, 46.3; H, 2.78; N, 24.0], identified by comparison with an authentic sample prepared by heating excess 1,1,3,3-tetramethoxypropane with 2,4-dinitrophenylhydrazine in dilute methanolic perchloric acid. Hence, one fragment of periodate oxidation with subsequent acid cleavage was malondialdehyde. No volatile carbonyl compound was detected during the conversion of II to III.

Without isolation the remaining five-carbon fragment was identified as the hitherto unreported⁴ 2,4-dihydroxy-3-pentanone (IV) by the following method. After removal of III, the acid hydroly-

(3) Prior to reaction with 2,4-dinitrophenylhydrazine it was necessary to remove the iodate ion present by means of its insoluble barium salt, because the iodate and the carbonyl reagent reacted to form tarry products.

(4) G. W. K. Cavill and D. H. Solomon, *J. Chem. Soc.*, 4426 (1955) describe the diacetate. G. Gál, et al., *Magyar Kém. Folyóirat*, 68, 5 (1958) [*Chem. Abs.*, 52, 18300i (1958)] report the oxime.

sate of II on treatment with periodate consumed one mole of the oxidant and produced one mole of acetaldehyde (estimated by bisulfite titration⁵ and isolated as the 2,4-dinitrophenylhydrazone,⁶ m.p. 136–150°) and 0.9 mole of lactic acid (estimated by base titration and identified *via* the *p*-bromophenacyl ester, m.p. 108–110°, by comparison with an authentic sample prepared from *dl*-lactic acid). The formation of these two fragments in high yield demonstrates that the periodate substrate must have been IV.

This sequence of reactions and compounds indicates that the compound $C_8H_{14}O_4$ has structure I, whose main features are completely compatible with the n.m.r. spectrum, presented in Table I.

It appears that this unique structure is actually a secondary reaction product resulting from acid catalyzed ring-closure of the natural "sugar." This postulate is supported by the observation that the crystalline anhydrosugar (I) is accompanied by a syrupy reducing sugar, presumably unchanged V.

(5) E. J. Conway, "Microdiffusion Analysis," Crosby Lockwood and Son, Ltd., London, Eng., 4th Edn., 1957, p. 278.

(6) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Thomas Y. Crowell Co., New York, N. Y., 1947, p. 400.

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ISOLATION AND CHARACTERIZATION OF MITIROMYCIN AND OTHER ANTIBIOTICS PRODUCED BY *STREPTOMYCES VERTICILLATUS* Sir:

Three soil isolates of *Streptomyces verticillatus*, Lederle strains AA-849, AB-286 and AB-929 were found to produce mixtures of ethyl acetate extractable antibiotics which were active in bacterial mouse protection tests. When purified preparations made from these cultures were compared by paper chromatography, they appeared to contain identical groups of antibiotics. The solvent system used consisted of benzene, methanol, 0.01 *M* phosphate buffer pH 6.8 (20:1:1 by vol.). Bioautography with *Bacillus subtilis* indicated six antibiotics, A₁, A₂, B, C, D and E with R_f values 0.75, 0.65, 0.36, 0.15, 0.09 and 0.01, respectively.

The extracts from strains AA-849 and AB-929 were resolved into fractions by partition chromatography with mixtures of benzene, ethyl acetate, methanol and phosphate buffer on Celite¹ and silicic acid columns. Five purple pigments, corresponding to A₂, B, C, D and E, were isolated in crystalline form. They were recrystallized from ethyl acetate-petroleum ether or from methanol. *trans*-Cinnamide also was isolated from a number of fractions.

At the highest level tested (500 mcg./ml.), compound A₂ showed comparatively low activity

(1) Johns-Manville Company brand of diatomaceous earth.