important to affect our qualitative conclusions concerning the role of the radical site.[12]

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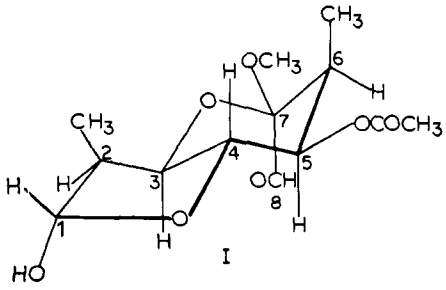
Chemistry of the Streptovaricins. IV. Structure of Varicinal A[1]

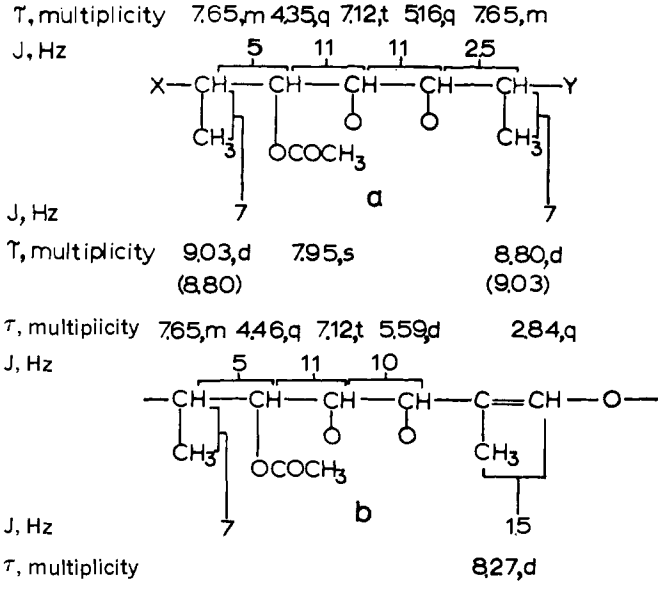
Sir:

We recently reported[2] that streptovaricin A ($C_{42}H_{53}NO_{16}$), a crystalline component of the antituberculosis streptovaricin antibiotic complex, on periodate oxidation gives prestreptovarone ($C_{29}H_{29}NO_9$), containing the chromophore of the antibiotic. We have now isolated the other, nonchromophoric product of this oxidation and assign structure I to the compound, which we have named varicinal A.



I

Although the electron impact produced mass spectrum of varicinal A ($C_{13}H_{20}O_7$. *Anal.* Found: C, 53.95; H, 7.17) does not contain a molecular ion, characteristic ions are found at *m/e* 271 (M − OH), 270 (M − H_2O), 257 (M − CH_3O), and 228 (M − HOAc), and the field ionization produced high-resolution mass spectrum[3,4] contains a molecular ion at the expected *m/e* 288.1201. Decoupling of the nuclear magnetic resonance spectrum (100 MHz, $CDCl_3$) of varicinal A indicates the structural unit a shown. Other protons are found at τ 0.39 (–CH=O, singlet), 4.96 (–CH(O)-O–, broad singlet), and 6.29 (–C(O)OCH_3).



The presence of two aldehyde groups (one masked as a hemiacetal) allows only two carbon skeletons, X = O=HCC(O)(OCH_3)–, Y = –CHO, in a, and the reverse. A decision is provided by the acetylation of varicinal A, which gives a dimeric acetate (mass spectral peak at *m/e* 660) containing the new structural unit b.

The formula (I) shown for varicinal A indicates the relative stereochemistry assigned from the coupling constants listed for partial formula a. The three all-*trans*-axial carbinyl protons of the pyranose ring are readily assigned (J = 11 Hz),[5] as is the adjacent *cis*-equatorial proton (J = 2.5 Hz). The hemiacetal and adjacent methine proton of the furanose ring must be *trans* to one another (J < 1 Hz),[6] but coupling constants do not allow assignment of the relative stereochemistry of the furanose methine proton (on C-2) and the adjacent bridgehead proton (H-3). Similarly, the stereochemistry of the methoxyl and formyl groups at C-7 remains unassigned.

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(3) Determined at the Purdue Mass Spectrometry Center.

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Chemistry of the Streptovaricins. V.[1] Structures of Streptovaricins A and C

Sir:

Structures I and II have recently been assigned to varicinal A[1] and prestreptovarone,[2,3] respectively, the products of periodate oxidation of the antibiotic streptovaricin A (III).[4]

The structural unit which leads to I can be located in the 100-MHz nmr spectrum of streptovaricin A in unit a_{III} [where the terminal carbons of prestreptovarone (II) are in the shaded area], identified in part by spin

(1) Paper III: R. J. Schacht and K. L. Rinehart, Jr., *J. Am. Chem. Soc.*, **89**, 2239 (1967).

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(2) K. L. Rinehart, Jr., C. E. Coverdale, and P. K. Martin, *ibid.*, **88**, 3150 (1966).

(3) Structure II has the *cis* linkage about the γ,δ-double bond of the dienamide group (rather than the *trans* linkage shown earlier),[2] in keeping with the H_{γ},H_{δ} coupling constant, 11.5 Hz. The same coupling constant is found in the 100-MHz spectrum of the intact antibiotic (III).

(4) K. L. Rinehart, Jr., P. K. Martin, and C. E. Coverdale, *J. Am. Chem. Soc.*, **88**, 3149 (1966).