inal hydrogenolysis mixture gave 3′-deoxyadenosine (cordycepin)[11,14] (**5**, B = adenine) and 2′-deoxyadenosine[11,12a] in a ratio of 9:1.

Treatment of the above iodo enol ester **3** with 1,5-diazabicyclo[4.3.0]nonene-5 (DBN) and other nonsaponifying bases gave the blocked (3-deoxy-β-D-*glycero*-pent-3-enofuranosyl) heterocycle plus the corresponding heterocycle-substituted furan derivative. Deblocking gave **6**,[11] mp 228–230°, which was hydrogenated to **5**[11,14] plus its 4′ epimer.[11,15]

Analogous reaction of 2′,3′-*O*-methoxyethylidenetubercidin[11] (**1**, Z = CH) gave **3**[11] (Z = CH; X = I; R = $COC[CH_3]_3$; R′ = $CH{=}C(OCOC[CH_3]_3)C[CH_3]_3$; mass spectrum calcd for $C_{33}H_{47}IN_4O_8$, 754.2339; found, 754.2376). Transformations of this material to give **4**,[11] mp 167° dec, **5**,[9b,11] and **6**,[11] mp 190–192° (B = 4-aminopyrrolo[2,3-*d*]pyrimidine) proceeded similarly with the exception that no 2′-deoxytubercidin was detected in the hydrogenolysis.

Isolation of intermediates involved in characterizing the interesting acyloxonium ion diacylation mechanism of enol ester formation, details of various other products formed, and applications of these useful intermediates in nucleoside chemistry will be reported in detail.

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Nitrosyl Transfer Reactions

Sir:

The recent literature contains several examples of reactions involving transfer of carbon monoxide from one metal atom to another.[1] We wish to report the first observations relating to nitrosyl transfer reactions.

Methanolic solutions of CoD_2PPh_3[2] rapidly absorb NO to yield a mononitrosyl adduct with ν_{NO} = 1710 cm^{-1} ($CHCl_3$ solution). The solution precipitates a solid of composition $CoNOD_2(MeOH)$,[3] with ν_{NO} = 1639 cm^{-1} (KBr); coordinated phosphine is not present. The similarity of the equatorial ligands and the NO stretching frequency of $CoNOD_2(MeOH)$ to those of $Co(en)_2NOCl^+ClO_4^-$ [4] and $CoNO(tet)$[5] suggests the Co–N–O moiety is bent in the dimethylglyoximate complex. Proton nmr of $CoNOD_2(MeOH)$ in $CDCl_3$ exhibits a methoxy resonance at a chemical shift identical with that of uncoordinated methanol; azeotropic distillation of methanol from a benzene solution of $CoNOD_2(MeOH)$ yields unsolvated $CoNOD_2$. All of the observations imply a large trans effect for NO, consistent with previous observations on bent nitrosyls.[6]

$CoNOD_2(MeOH)$ reacts with $CoCl_2L_2$ and L (L = PPh_3) (2:1:2 molar ratio) in ethanol to yield $CoClD_2L$ (1 mol), CoD_2L (1 mol), and an equilibrium mixture[7]

$$Co(NO)_2L_2{}^+Cl^- \rightleftharpoons Co(NO)_2LCl + L$$

$NaBPh_4$ displaces this equilibrium to the left by quantitatively precipitating $Co(NO)_2L_2{}^+BPh_4^-$. The overall reaction (1) involves the transfer of two nitrosyl groups and a chlorine atom. Since the NO donor reagent is a mononitrosyl, it is natural to consider a stepwise process. The intermediacy of a mononitrosyl in reaction 1 is suggested by the observation that $Co(NO)Cl_2L_2$[8] reacts with $CoNOD_2(MeOH)$ and L (1:1:1 mol ratio) to form the dinitrosyl (2). No Ph_3PO is detected after these reactions, indicating the absence of free NO. An alternative mechanism involving initiation of the reaction by catalytic amounts of the halogen acceptor[9] CoD_2 is ruled out by the observation that neither CoD_2 nor CoD_2L will reduce $CoCl_2L_2$.

$$2CoNOD_2(MeOH) + CoCl_2L_2 + 2L \longrightarrow CoD_2L + CoClD_2L + Co(NO)_2L_2Cl \quad (1)$$

$$CoNOD_2 + Co(NO)Cl_2L_2 \xrightarrow{L} CoClD_2L + Co(NO)_2L_2Cl \quad (2)$$

Square-pyramidal cobalt complexes with CH_3 or bent NO in the apical position exhibit many similarities. Foremost is the common ambiguity in assignment of oxidation states: $CH_3(+1)$, CH_3, or $CH_3(-1)$ *vs.* NO(+1), NO, or NO(−1). Both groups have very high trans effects, sometimes allowing isolation of the complex with the trans position unoccupied.[5,10] $CoCH_3D_2$ is dimeric,[11] resonances of nonequivalent dimethylglyoximate methyl groups being apparent below −12°. The proton nmr of $CoNOD_2(MeOH)$ shows only one resonance for dimethylglyoximate methyl groups even at −90°, implying an even stronger trans effect for bent NO than for CH_3. Finally the nitrosyl transfer reaction observed here mimics the known alkyl transfer reactions of alkyl cobalt Schiff base complexes.[12]

Although simple nitrosyl transfer must occur at some stage in reaction 1, it seems likely that the efficacy of $CoNOD_2(MeOH)$ as a nitrosyl source is related to the fact that the CoD_2 produced can also function as a halogen acceptor. Consistent with this idea, we find that nitrosyl–halogen interchange appears to be a rather general reaction. For example

$$CoNOD_2(MeOH) + NiCl_2L_2 \longrightarrow {}^1/_2[Ni(NO)ClL]_2 + CoClD_2L \xrightarrow{L} Ni(NO)ClL_2$$

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Nitric oxide alone does not react with $NiCl_2L_2$ to produce this nickel nitrosyl halide.[13]

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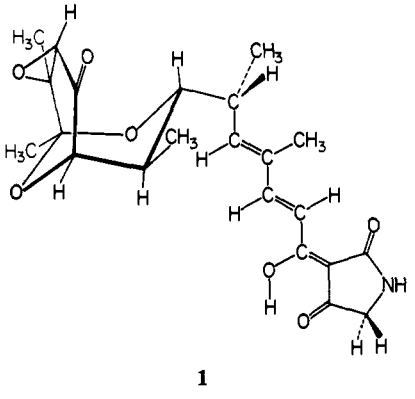
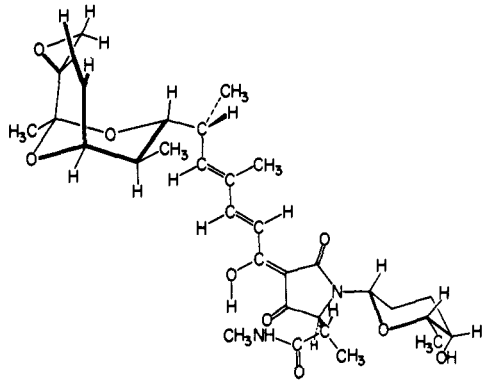
X-Ray Structure of Tirandamycic Acid *p*-Bromophenacyl Ester. Complete Stereochemical Assignments of Tirandamycin and Streptolydigin

Sir:

Gross structures have been assigned earlier to the two acyltetramic acid antibiotics tirandamycin[1] and streptolydigin,[2] which have stimulated considerable recent interest on account of their modes of action, especially their inhibition of RNA polymerase.[3] We report here the complete X-ray determination of the structure of the *p*-bromophenacyl ester of tirandamycic acid,[1] which completes the absolute stereochemical assignment of tirandamycin as **1**. We also report here the conversion of tirandamycic acid and streptolic acid[4] to a common derivative retaining the stereochemistry of both acids, as well as additional stereochemical data on the ydiginic acid[5] portion of streptolydigin; together, these results allow the complete stereochemical assignment of streptolydigin as **2**.



1



2

The *p*-bromophenacyl ester of tirandamycic acid (**3**) was prepared by reaction of the sodium salt of the acid with *p*-bromophenacyl bromide, purified over silica gel, and crystallized from ethanol: $C_{26}H_{29}BrO_7$;[6,7] mp 173–183°; $[\alpha]^{25}D$ +50° (*c* 1.09, $CHCl_3$). The crystals are monoclinic, space group $P2_1$ with a = 17.603, b = 8.400, and c = 8.673 Å, and β = 90.73°. Three-dimensional X-ray diffraction intensity data were gathered on a computer-controlled diffractometer using nickel-filtered Cu radiation. The data (2603 reflections) were corrected for systematic errors including absorption.[8] A trial Br position was obtained by computerized direct methods. A three-dimensional electron density map, phased using this Br, contained images of two superimposed molecules, as expected. The superimposed images were sorted out by analysis of distances and angles, and without reference to the previously assigned stereochemistry or structure of tirandamycic acid. In this manner a partial trial structure (17 atoms and Br) was obtained from the initial map. Full separation of the images required two more electron density calculations. Atomic positions and first isotropic, then anisotropic, thermal parameters refined by least squares to an agreement factor R ($=\Sigma||F_o| - |F_c||/\Sigma F_o$) of 0.102 without including anomalous dispersion. At this point, the correct enantiomer was determined by Bijvoet's method.[9] Structure factors were calculated for both enantiomers, and 15 reflections most affected by anomalous dispersion were selected for accurate measurement of $I(h,k,l)$, $I(-h,k,-l)$, $I(-h,-k,-l)$, and $I(h,-k,l)$. All 15 clearly indicated the enantiomer shown in Figure 1. Additional least-squares refinement, with anomalous dispersion effects included, reduced R to 0.083. Details of the crystallographic investigation will be published.[10]

The X-ray results agree perfectly with previous structural assignments on tirandamycic acid.[1] The assignment of the stereochemistry of the bromo ester as that shown in Figure 1 (6*R*,7*R*,8*R*,9*S*,11*R*,12*S*,13*S*) completes the absolute stereochemical assignment of tirandamycin as **1**.

The α-keto epoxide group of tirandamycic acid (**3**) was reduced by the procedure of Wharton and Bohlen[11]

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