to give 4-oxazolines (**4**, R″ = H) which open spontaneously to the dipoles **3** at room temperature. Further reduction occurs in the absence of dipolarophiles, but in the presence of DMAD, **3d** affords a single cycloadduct **8d** in excellent yield.[11] Attempts to purify the 2,5-dihydropyrrole are complicated by double-bond migration and aromatization. For this reason, related DMAD cycloadducts have been assayed after aromatization to the pyrroles **9** with DDQ (Table II).[12] The trans stereochemistry for **8d** is assigned by NMR comparisons with related dihydropyrroles.[3c,d] The corresponding dipole geometry **3d** is also supported by formation of the *N*-phenylmaleiimide adduct **10**.[13] An experiment where **3d** is generated from **4d** in the presence of methyl acrylate again affords a 2 + 3 cycloadduct **7d** assumed to have similar stereochemistry. Several related acrylate adducts are likewise formed as single stereoisomers (Table II).

Our findings suggest that the relative stability of valence bond tautomers **1–4** is strongly influenced by the presence of a substituent R″ at C_4. When R″ = alkyl, aryl, etc., **4** resists opening to dipole **3** and there are several examples where **4** can be made by heating the aziridine **2**.[7,8] For R″ = H, however, ring opening of **4** to **3** is rapid at room temperature. Valence bond tautomerization of the corresponding aziridines **2** is much slower and requires ≥ca. 60 °C, so the relative stability of **4** vs. **2** (R″ = H) now favors the aziridine **2**. We have no comment on the reasons for the reversal of 4-oxazoline vs. aziridine stability, but the greater ease of oxazoline ring cleavage to **3** when R″ = H compared to R″ = aryl, alkyl, etc. can be attributed to eclipsing effects which destabilize the planar dipole when R″ is larger than hydrogen.

We expect that the 4-oxazoline route to azomethine ylides **3** demonstrated here[16] will prove superior to the aziridine approach in most cases, especially when alkyl substitution on the dipole is desired. Precursor oxazoles are easily made and modified, and a variety of applications of this technique are under investigation. We also note that controlled reduction of imidate salts to the aldehyde oxidation state is central to our procedure. The potential of the $PhSiH_3/CsF$ reagent for this purpose in other synthetic applications is clear.

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Registry No. 3 (R = Me; R′ = R‴ = Ph; R″ = H), 102537-03-1; **3** (R = R‴ = Me; R′ = Ph; R″ = H), 102537-04-2; **3** (R = Me; R′ = Ph; R″ = H; R‴ = OC_2H_5), 102537-05-3; **3** (R = Me; R′ = Ph; R″ = R‴ = H), 102537-06-4; **3** (R = R′ = Me; R″ = H; R‴ = OC_2H_5), 102537-07-5; **3** (R = R′ = Me; R″ = H; R‴ = Ph), 102537-08-6; **4** (R = R′ = Me; R″ = R‴ = Ph), 102536-93-6; **4** (R = R′ = R″ = R‴ = Me), 102536-94-7; **4** (R = R″ = Me; R′ = R‴ = Ph), 102536-95-8; **5** (R = H; R′ = Me; R″ = R‴ = Ph), 102536-90-3; **5** (R = H; R′ = R″ = R‴ = Me), 102536-91-4; **5** (R = H; R′ = R‴ = Ph; R″ = Me), 102536-92-5; **5** (R = R″ = H; R′ = R‴ = Ph), 59973-27-2; **5** (R = R″ = H; R′ = Ph; R‴ = Me), 102536-99-2; **5** (R = R″ = H; R′ = Ph; R‴ = OC_2H_5), 102537-00-8; **5** (R = R″ = R‴ = H; R′ = Ph), 64001-60-1; **5** (R = R″ = H; R′ = CH_3; R‴ = OC_2H_5), 102537-01-9; **5** (R = R″ = H; R′ = CH_3; R‴ = Ph), 102537-02-0; **5** (R = R′ = Me; R″ = R‴ = Ph), 102537-21-3; **5** (R = R′ = R″ = R‴ = Me), 102537-22-4; **5** (R = R″ = Me; R′ = R‴ = Ph), 102537-23-5; **5** (R = Me; R′ = R‴ = Ph; R″ = H), 54901-89-2; **5** (R = R‴ = Me; R′ = Ph; R″ = H), 102537-24-6; **5** (R = Me; R′ = Ph; R″ = H; R‴ = OC_2H_5), 102537-25-7; **5** (R = Me; R′ = Ph; R″ = R‴ = H), 102537-26-8; **5** (R = R′ = Me; R″ = H; R‴ = OC_2H_5), 102586-38-9; **5** (R = R′ = Me; R″ = H; R‴ = Ph), 64988-40-5; **6a**, 102536-96-9; **6b**, 102536-97-0; **6c**, 102536-98-1; **7** (R = Me; R′ = R‴ = Ph), 102537-15-5; **7** (R = R‴ = Me; R′ = Ph), 102537-16-6; **7** (R = Me; R′ = Ph; R‴ = OC_2H_5), 102537-17-7; **7** (R = Me; R′ = Ph; R‴ = H), 102537-18-8; **7** (R = R′ = Me; R‴ = OC_2H_5), 102537-19-9; **7** (R = R′ = Me; R‴ = Ph), 102537-20-2; **8d**, 102537-09-7; **9** (R = Me; R′ = R‴ = Ph), 102537-10-0; **9** (R = R‴ = Me; R′ = Ph), 102537-11-1; **9** (R = Me; R′ = Ph; R‴ = OC_2H_5), 102537-12-2; **9** (R = R′ = Me; R‴ = OC_2H_5), 102537-13-3; **9** (R = R′ = Me; R‴ = Ph), 102537-14-4; DMAD, 762-42-5; CH_2=$CHCO_2Me$, 96-33-3.

(11) **8d**: ^1H NMR (CD_3CN, ppm) 8.09–7.24 (10 H, m), 5.89 (1 H, d, *J* = 5.7 Hz), 5.22 (1 H d, *J* = 5.7 Hz), 3.55 (3 H, s), 3.54 (3 H, s), 2.14 (3 H, s).

(12) For example, **9d**: ^1H NMR ($CDCl_3$, ppm) 7.8–7.45 (10 H, m), 3.57 (3 H, s), 3.53 (3 H, s), 3.23 (3 H, s).

(13) **10**: ^1H NMR ($CDCl_3$, ppm) H_2 at 5.54 (s, $J_{2,3} \sim 0$ Hz); H_5 at 4.9 (d, $J_{4,5}$ = 9.1 Hz); see ref 3c,e for analogous structures.

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(15) Note that **3** is not necessarily formed from **2** since two isomeric dipoles can be formed by conrotatory aziridine opening, both of which would give **8**.

(16) Typical procedure: methyl triflate (0.249 mmol) was added to a solution of 5-methyl-2-phenyloxazole (0.226 mmol) in 3 mL of dry acetonitrile. After the mixture was stirred for 2 h at room temperature, phenyl silane (0.339 mmol) and methyl acrylate (0.747 mol) were added and this mixture was added by cannula to anhydrous cesium fluoride (0.452 mmol) in acetonitrile (4 mL). After 2 h, solvent removal and flash chromatography gave **7e** (0.197 mmol, 87%) as a white solid (mp 54–55 °C).

Stereochemistry of the 5-(*p*-Aminophenyl)-1,2,3,4-tetrahydroxypentane Portion of Methanopterin

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Methanopterin (Figure 1), a recently characterized cofactor[1,2] involved in the biological reduction of CO_2 to CH_4,[3,4] is currently postulated to function in its reduced state (tetrahydromethanopterin) as a C_1 carrier at the oxidation levels of formyl, methenyl, methylene, and methyl in a manner similar to that described for folic acid.[5] Recent work, aimed at defining the biosynthesis of this coenzyme, has shown that the pterin ring most likely arises from guanosine triphosphate[6,7] and that the 7-methyl group arises from methionine.[8] The aromatic portion of the 5-(*p*-aminophenyl)-1,2,3,4-tetrahydroxypentane has been shown to arise from *p*-aminobenzoic acid[6] and the side chain polyol from a pentose[6,8] with the C-1 through C-5 carbons of the side chain arising from the C-5 through C-1 carbons of the pentose. It is proposed that the reaction proceeds by the addition of the para carbon opposite the amino group of the *p*-aminobenzoic acid to the C-1 of the pentose with the subsequent loss of CO_2 in a reaction sequence analogous to that observed in the formation of indoleglycerol phosphate from phosphoribosyl anthranilate during the biosynthesis of tryptophan.[9] Since the configuration of carbon atoms 2–4 of the pentose is not expected to change during this type of reaction, the determination of the stereochemistry of the asymmetric carbons 2–4 of the 5-(*p*-aminophenyl)-1,2,3,4-tetrahydroxypentane will define which pentose is involved in the biosynthesis. This stereochemistry was determined to be ribo by the synthesis of each of the four possible stereoisomers. Only the ribose-derived isomer has the same chromatographic properties as the isomer present in methanogenic bacteria.

Each of the stereoisomers was prepared by the synthetic scheme outlined in Figure 2 starting with the known pentoses D-arabinose, D-ribose, D-xylose, and D-lyxose. The conversion of the pentoses into their diethyl dithioacetal derivatives (step a) and the subsequent conversion of these derivatives into their diisopropylidene derivatives (step b) have been previously described.[10-12] The

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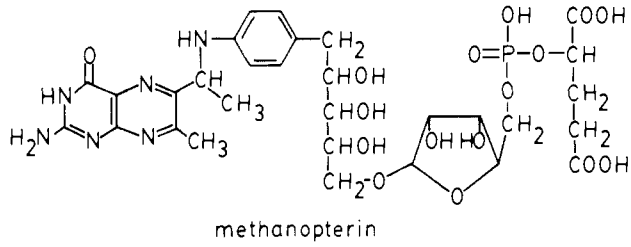

Figure 1. Chemical structure of methanopterin.

resulting diisopropylidene diethyl dithioacetal pentose derivatives were converted into the respective di-*O*-isopropylidene aldehydes (step c) by cleavage in the presence of mercury chloride and cadmium carbonate as described by English[13] with the exception that the chloroform extract of the reaction mixture was washed with 10% KI to remove the mercury salts[14] and the products were purified by chromatography on silica gel.[12] The resulting aldehydes were coupled at −78 °C in diethyl ether with [*N*,*N*-bis(trimethylsilyl)-*p*-anilinyl]lithium which was prepared from *p*-bromo-*N*,*N*-bis(trimethylsilyl)aniline (step d) as described by Pratt.[15] After 12 h, the reaction mixtures were warmed to room temperature, treated with methanol saturated with ammonium chloride, and washed with water. The resulting 1,2,3,4-di-*O*-isopropylidene-5-(*p*-aminophenyl)-1,2,3,4,5-pentahydroxypentanes were then reduced with an excess of $LiAlH_4$ (5×) at 80 °C in ether in a sealed tube for 48 h[16] followed by acid hydrolysis with 1 M HCl for 1 h at 100 °C to give the final product which was purified by preparative thin-layer chromatography.

Samples of 5-(*p*-aminophenyl)-1,2,3,4-tetrahydroxypentane were isolated by the oxidative cleavage of tetrahydromethanopterin isolated from *Methanobacterium formicicum* and rumen isolate 10-16B as previously described.[6,17]

The synthetic products, as well as the samples isolated from the methanogenic bacteria, were converted into their pentatrifluoroacetyl derivatives by heating at 60 °C for 2 h with an equal mixture of methylene chloride and trifluoroacetic anhydride (v/v). After evaporation of the solvents, the derivatives were dissolved in methylene chloride and separated by gas chromatography on a 0.32 × 305 cm glass column packed with 3% SP-2100. When the temperature was programmed from 150 °C at 6 °C/min the retention times for the ribose, arabinose, xylose, and lyxose isomers were 3.64, 3.74, 3.81, and 4.02 min, respectively. The sample isolated from the methanogenic bacteria had a retention time of 3.64 min and cochromatographed with the ribose-derived standard. This same order has been observed for the elution of the trifluoroacetyl derivatives of the pentitols during gas chromatography.[18,19]

The mass spectrum of the derivatized synthetic sample which was derived from D-ribose was recorded at 70 eV on a VG 70-70E-HF gas chromatograph–mass spectrometer and was identical with that of the derivative of the 5-(*p*-aminophenyl)-1,2,3,4-tetrahydroxypentane isolated from the bacteria. The major observed ions (their observed intensities are in parentheses) were at *m*/*z* 69 (44), 107 (24), 132 (14), 202 (100), 226 (55), 252 (32), 240 (16), 366 (7), 393 (19), and M^+ 707 (15). The mass spectrum of the pentatrifluoroacetyl derivative for each of the other stereoisomers was essentially identical with that of the ribose isomer except for small variations in the intensities of the *m*/*z* 69 and 107 ions.

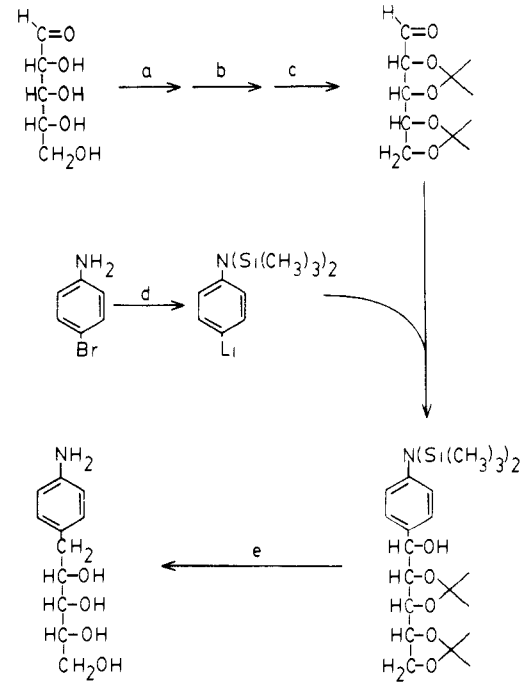

Figure 2. Synthetic scheme for the synthesis of 5-(*p*-aminophenyl)-1,2,3,4-tetrahydroxypentane of known stereochemistry starting from pentoses.

This work establishes methanopterin to be the third example of a coenzyme in nature having a polyol side chain with the ribitol stereochemistry, the other examples being riboflavin[20] and coenzyme F_{420}.[21]

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Multiple Intermediates Generate Fluorophore-Derived Light in the Oxalate/Peroxide Chemiluminescence System[1]

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We have obtained evidence for new mechanistic features of the reaction[2] of bis(2,4,6-trichlorophenyl) oxalate (TCPO) with hydrogen peroxide and triethylamine (TEA) in the presence of 9,10-diphenylanthracene (DPA) in ethyl acetate as solvent. Chemiluminescence is generated by at least two intermediate compounds X and Y which produce the same singlet excited state

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