trations eq 3 begins to dominate and the $O_2(^1\Delta g)$ concentration decreases. The variation of IR emission with $N(C_2H_5)_3$ concentration provides powerful additional support for the presence of $O_2(^1\Delta g)$.

When the triethylamine concentration is held constant at ~324 ppm and the ozone concentration was increased from 65 ppm, the $O_2(^1\Delta g)$ concentration increases with increasing ozone concentration as indicated by the 1.27-μm emission and reaches a plateau maximum from an O_3 concentration of 270-480 ppm. The $O_2(^1\Delta g)$ concentration decreased above an O_3 concentration of 480 ppm as the influence of eq 2 was felt.

Previous work in solution demonstrated that triethylamine oxide was the major organic product in the reaction of ozone with triethylamine.[10] Product studies are currently under way to characterize the product of the ozone-triethylamine reaction in the gas phase.

The results reported here indicate that the use of the 1.27-μm emission of $O_2(^1\Delta g)$ provides a powerful tool for investigating the question of the production of $O_2(^1\Delta g)$ in the gas-phase reactions of O_3 with organic substances. We plan to extend these studies to other examples where $O_2(^1\Delta g)$ is expected to be produced directly by reaction of O_3 with substrates such as certain olefins and sulfoxides, as well as to cases where O_3 reactions produce intermediates which have been shown to decompose to give an oxidized substrate and $O_2(^1\Delta g)$. The current results add support to the suggestion made by Pitts and co-workers,[10] ourselves,[2,6b,11] and others[12] that a variety of $O_2(^1\Delta g)$ generation processes can operate in polluted atmospheres to jointly contribute to the production of a significant concentration of $O_2(^1\Delta g)$.

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Biosynthesis of 7,8-Didemethyl-8-hydroxy-5-deazariboflavin, the Chromophoric Moiety of Coenzyme F_{420}

Quang Le Van, Bruno Schwarzkopf, and Adelbert Bacher*

Lehrstuhl für Organische Chemie und Biochemie
Technische Universität
München, D-8046 Garching, West Germany

Paul J. Keller, Sungsook Lee, and Heinz G. Floss*

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

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Methanogenic bacteria contain a variety of unusual cofactors such as coenzyme F_{420},[1] coenzyme F_{430},[2] methanopterin,[3] methanofuran,[4] and coenzyme M,[5] which are involved in the process of methanogenesis. We have shown earlier that cultures of *Methanobacterium thermoautotrophicum* excrete substantial amounts of 7,8-didemethyl-8-hydroxy-5-deazariboflavin (**4**, Figure 1), the chromophoric moiety of coenzyme F_{420}, into the culture medium.[6]

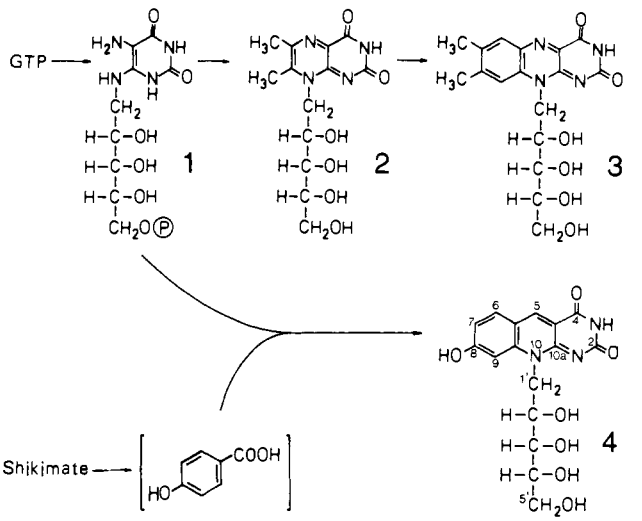

Figure 1. Proposed pathway for the biosynthesis of 7,8-didemethyl-8-hydroxy-5-deazariboflavin (**4**).

The structural similarity of riboflavin (**3**) and its deaza analogue **4** raises the question whether the two types of chromophores are produced by similar metabolic pathways. The biosynthesis of riboflavin has been studied extensively in eubacteria and in fungi.[7] The pathway starts from GTP and leads through several steps to 5-amino-6-(ribitylamino)-2,4(1*H*,3*H*)-pyrimidinedione 5′-phosphate (**1**) (Figure 1).[8] The addition of a pentose-derived four-carbon moiety,[9] which could be isolated only recently,[10] yields the pteridine derivative, 6,7-dimethyl-8-ribityllumazine (**2**). The xylene ring of riboflavin then arises by an unusual dismutation of the lumazine.[7]

Little is known about the biosynthesis of deazaflavins. Tracer studies have shown the incorporation of ^{14}C into coenzyme F_{420} from position 2 but not from position 8 of guanine.[11] Isotope from [1-^{13}C]glycine was incorporated into position 10a of the deazaflavin chromophore.[12] These data suggest that the pyrimidine ring of deazaflavins is biosynthesized from a purine in analogy with riboflavin. However, the origin of the carbocyclic ring of deazaflavins is unknown. It was only shown that tyrosine and the methyl group of methionine are not incorporated.[11]

^{13}C incorporation studies have been useful in the elucidation of the biogenesis of the xylene ring of riboflavin using a variety of labeled precursors.[9] Similar studies in *Methanobacteria* are limited by the poor uptake of complex nutrients. However, detailed information can be obtained even with simple precursors, such as acetate, by pattern recognition methods.[9] With this strategy in mind we have studied the incorporation of [1-^{13}C]acetate in *M. thermoautotrophicum* Marburg. The organism was grown at 65 °C in 14 L of a minimal medium supplemented with 5 mM [1-^{13}C]acetate in an atmosphere containing 20% CO_2 and 80% H_2. The pH of the culture medium was maintained at 6.0 by the addition of sodium bicarbonate. **4** was isolated from the culture

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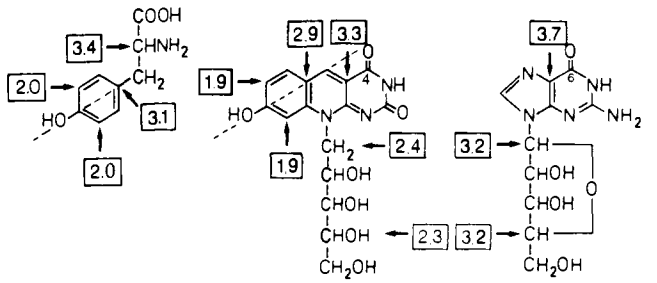

Figure 2. ^{13}C abundances in metabolites isolated from cultures of *Methanobacterium thermoautotrophicum* grown in the presence of [1-^{13}C]acetate. Numbers indicate relative ^{13}C abundances. Carbon atoms without designations have ^{13}C abundances of 0.9–1.2.

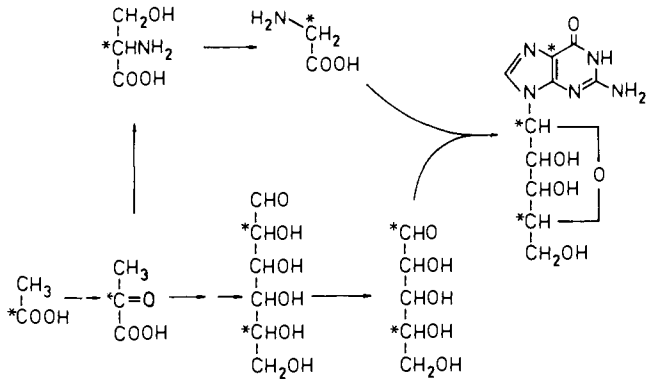

Figure 3. Carbohydrate metabolism in *Methanobacterium thermoautotrophicum*. Asterisks signify ^{13}C-labeled positions.

medium by adsorption to a column of Dowex 1. The compound was purified by chromatography on QUAE Sephadex followed by reversed-phase HPLC.[6]

The bacterial cells were treated with 0.1 M NaOH, and the nucleotides resulting from the hydrolysis of RNA were isolated by anion exchange chromatography.[13] Treatment of 2′,3′-GMP with phosphatase afforded guanosine. Tyrosine was obtained from cellular protein after acid hydrolysis by a sequence of anion exchange chromatography and HPLC.

Proton-decoupled ^{13}C NMR spectra of all isolated compounds were measured at 7.1 T on a Bruker WM-300 NMR spectrometer. Isotope enrichments were calculated from integrals by comparison with the spectra of natural-abundance material. Signal assignments for 8-hydroxy-7,8-didemethyl-5-deazariboflavin were based on chemical shift considerations, NMR titration studies, analysis of long-range ^{1}H–^{13}C couplings, and low-power single-frequency ^{1}H-decoupling experiments.

^{13}C abundances of labeled carbon atoms are shown in Figure 2. It is immediately apparent that no substantial randomization of the isotope has occurred in agreement with observations on amino acid biosynthesis in *Methanospirillum hungatei*.[14] The labeling pattern of the ribose moiety of guanosine is in line with accepted knowledge on carbohydrate metabolism pathways operating in methanogenic bacteria (Figure 3).[15] The labeling pattern of tyrosine is easily explained by the shikimic acid pathway on the basis of the carbohydrate labeling pattern described above.

The labeling pattern of **4** suggests that the ribitol moiety originates by reduction of a ribose moiety and that the pyrimidine ring is derived from the pyrimidine ring of a purine precursor. The carbocyclic rings of **4** and of tyrosine show identical patterns of ^{13}C enrichment. Since tyrosine has been ruled out as precursor,[11] we are left with the hypothesis that the carbocyclic ring of **4** is derived from another product of the shikimate pathway. **4** shows a quasi-symmetrical distribution of isotope indicated by the dashed line in Figure 2, and, hence, the direct precursor should be a symmetrical aromatic molecule, such as 4-hydroxybenzoate.

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Chiral Complexes Polymerize Methacrylate Esters To Give Helical Polymers That Mutarotate by Uncoiling[1]

Donald J. Cram* and Dotsevi Y. Sogah

Department of Chemistry and Biochemistry of the University of California Los Angeles, California 90024
E. I. duPont de Nemours and Co. Central Research and Development Experimental Station, Wilmington, Delaware 19898

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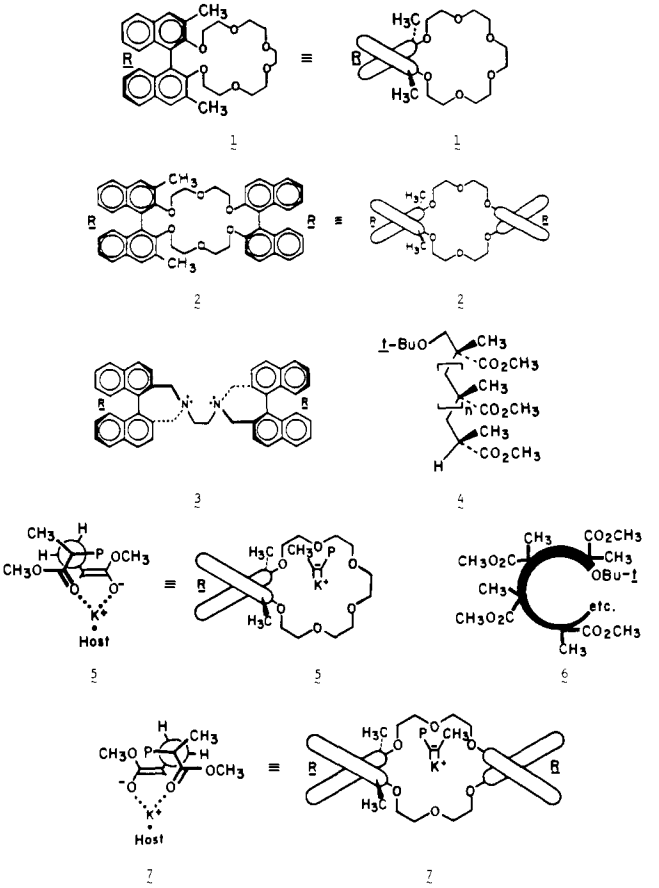
Previous work demonstrated that potassium bases complexed to chiral hosts (*R*)-**1** and (*R*,*R*)-**2** catalyzed Michael additions of carbon acids to α,β-unsaturated esters and ketones with high asymmetric induction, yields, and turnover numbers.[2] In other work, butyllithium complexed to chiral ethylenediamine, (*R*,*R*)-**3**,



added to benzaldehyde to give 1-phenyl-1-pentanol with high asymmetric induction.[3] The preferred configurations of the products were interpreted in terms of differences in steric interactions between catalyst and reactants in diastereomeric transition states. Since anionic polymerization of methacrylate esters is a

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