

and vinylic protons broadened out extensively presumably through fluxional isomerism in the allylic mercurial **7**.¹¹ Treatment of the mercurated reaction mixture with aqueous KCl solution at -20 to 0 °C and silica gel chromatography at -50 °C gave an $\sim 40\%$ yield of hydroperoxy mercurial **9** which on subsequent treatment with bromine gave the allylic bromohydroperoxide **10**, but not **6a** nor **6b**.

The novel mercurio-1,2-dioxetanes **2a** and **2b** reported here are the first examples of an unprecedented cycloperoxymercuration leading to four-membered rings.⁵ Regioselectivity⁵ and the Baldwin rules¹² predict that formation of the 1,2-dioxetane ring should be preferred over the 1,2-dioxolane ring in the mercuration of **1**; however, in view of the ring strain in **2a** and **2b** the major process is allylic mercuration. Work is in progress to suppress this menacing side reaction by cyclomercurating allylic hydroperoxides **1** without allylic hydrogens.

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References and Notes

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- (7) Distilled at 20 °C (0.01 mm); yellow liquid which solidifies at -20 °C, but could not be recrystallized; $^1\text{H NMR}$ (CCl_4 , Me_4Si) δ 1.53 (s, CH_3 , 6 H), 1.61 (s, CH_3 , 3 H), and 3.30 and 3.97 ppm (AB q, $J = 10$ Hz, CH_2 , 2 H); IR (CCl_4) 3030, 2980, 1456, 1387, 1380, 1373, 1232, 797, and 740 cm^{-1} . On heating at 80 °C **6a** decomposes quantitatively into acetone and bromoacetone.
- (8) Yellow liquid; $^1\text{H NMR}$ (CCl_4 , Me_4Si) δ 1.61 (s, CH_3 , 6 H) and 3.82 and 4.08 ppm (AB q, $J = 11$ Hz, CH_2 , 4 H); IR (CCl_4) 2990, 2965, 1430, 1383, 1370, and 1295 cm^{-1} . On heating at 80 °C **6b** decomposes quantitatively into acetone and 1,3-dibromo-2-propanone.
- (9) The dibromohydroperoxide, prepared by bromination of **1**, was added to silver trifluoroacetate in CH_2Cl_2 at 0 °C under stirring. After workup a yellow oil was obtained and separated by silica gel chromatography at -35 °C to afford **6a** in 30% yield.
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A Low Spin Manganocene and Its Novel Anionic Derivative. Synthesis and Characterization of Decamethylmanganocene Complexes

Sir:

Manganocene is unique among the first row transition metal metallocenes in that it has a high spin ($^6\text{A}_{1g}$) ground electronic configuration, behaves antiferromagnetically as a crystalline solid, and undergoes reactions characteristic of ionic cyclopentadienide complexes.^{1,2} Detailed EPR and magnetic studies of 1,1'-dimethylmanganocene in both solution^{3a} and the solid state^{3b} indicate an equilibrium between high spin ($S = 5/2$) and low spin ($S = 1/2$) electronic states, with the low spin configura-

tion predominating at lower temperature. It was inferred that manganocene is close to the high spin-low spin crossover point and that the substitution of an electron-donating methyl group on each ring sufficiently increases the donor character of the ligand to stabilize the low spin configuration.

We wish to report our synthetic and initial physical studies of decamethylmanganocene (**1**). The reaction of lithium pentamethylcyclopentadienide⁴ in tetrahydrofuran (THF) with anhydrous manganese(II) chloride, followed by vacuum sublimation (100 °C (10^{-5} Torr)) and recrystallization from hexane, gave good yields of pure **1** as air-sensitive, red-orange crystals.⁵

Magnetic susceptibility measurements on solid samples of **1** from 4 to 116 K indicate simple Curie behavior ($C_i = 0.59$) with a $\mu_{\text{eff}} = 2.16 \pm 0.1 \mu_{\text{B}}$ at 116 K. In toluene solution at 313 K, a $\mu_{\text{eff}} = 1.97 \pm 0.1 \mu_{\text{B}}$ was determined using the Evans NMR method.⁶ These results are consistent with the formulation of a low spin ($S = 1/2$) electronic configuration for **1**, with no evidence for thermal population of the high spin ($S = 5/2$) state up to room temperature. These data, in conjunction with infrared, NMR,⁷ EPR, and preliminary x-ray crystallographic⁸ results indicate that **1** is a normal metallocene, and is isostructural and isoelectronic with the ferricenium ion.

This analogy suggests that **1** might be readily reduced to a d^6 , manganese(I) anionic derivative that is isoelectronic with ferrocene and π -benzene- π -cyclopentadienylmanganese.⁹ No such metallocene anions have been isolated and it has been suggested¹⁰ that they might be too "electron rich" to be readily isolable. While the electrochemical reduction of nickelocene, cobaltocene, chromocene, and vanadocene has recently been reported,¹¹ the resulting anions were neither isolated nor characterized in solution. The closed-shell, 18-electron sandwich complex, bis(η -benzene)vanadium(-I) anion, has been characterized in solution by $^1\text{H NMR}$ spectroscopy.¹² An EPR spectrum of the 19-electron (η -cyclopentadienyl)(η -cycloheptatrienyl)chromium anion has also been reported.¹³ However, neither of these reduced species were sufficiently stable to allow isolation.

The cyclic voltammogram of **1** exhibits both a reversible one-electron reduction and oxidation.¹⁴ The reaction of **1** with 1 equiv of sodium naphthalide in THF yielded a dark red solution of the decamethylmanganocene anion (**2**). From this solution, an orange, crystalline sodium salt of **2** containing coordinated THF was isolated. This material readily loses THF at room temperature in vacuo to yield $\text{Na}[(\text{C}_5\text{Me}_5)_2\text{Mn}]$ as a pyrophoric orange powder.^{15a} The ^1H and ^{13}C NMR spectra^{15b} of **2** are consistent with the formulation of a diamagnetic, closed-shell metallocene.

In its reactions with protic acids and alkyl halides, **2** behaves as a strong one-electron reducing agent to yield only **1** with no evidence of products derived from addition of electrophile to the ring. Reaction of **2** with excess FeCl_2 in THF gives only **1**, with no detectable amount of decamethylferrocene. This indicates that both **1** and **2** are inert toward ring exchange reactions that are characteristic of manganocene.¹

These preliminary results suggest that the addition of five electron-donating methyl substituents to the cyclopentadienyl ligands results in a significantly increased crystal field splitting in planar metallocenes. Detailed spectral and structural studies of complexes **1** and **2** are underway in an effort to more completely describe their electronic structures.¹⁶ These, and related studies on other decamethylmetallocenes,¹⁶ will be important in assessing the *electronic* effects of methyl substitution on the structure and reactivity of coordinatively unsaturated and highly reduced derivatives of the early transition metals.

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Biosynthesis of the Nucleoside Skeleton of Polyoxins¹

Sir:

Previous studies from our laboratory have shown that the 5-substituted pyrimidines of the polyoxin antibiotics² are derived from uracil and C-3 of serine. The biosynthesis of the 5-substituted uracils is not dependent on thymidylate synthetase.³ The biosynthesis of the two side-chain amino acids was also studied in detail.⁴⁻⁶ However, the biosynthesis of 5-amino-5-deoxy-D-allofuranoseuronic acid is not understood. This unique sugar amino acid is the common constituent of all the polyoxins. Previous experiments³ have shown that ^{14}C -labeled glucose, ribose, and glycerol were incorporated into the uronic acid. However, with the exception of C-6', the distribution of ^{14}C could not be determined because a practical carbon-to-carbon degradation method was not available. This difficulty has now been overcome by utilizing $[1-^{13}\text{C}]$ glucose and ^{13}C NMR analysis. In addition, we have studied the biosynthesis of the nucleoside skeleton of the polyoxins in detail using ^{14}C -labeled compounds including $[3-^{14}\text{C}]$ glycerate and $[U-^{14}\text{C}]$ uridine. In this paper, we propose a novel biosynthetic pathway for the uronic acid moiety of **1** in Scheme I. This in-

Scheme I. Proposed biosynthetic pathway for the nucleoside skeleton of the polyoxins. Asterisk shows the ^{13}C enrichment from D- $[1-^{13}\text{C}]$ glucose. Incorporation stage of the one-carbon unit into C-7 is not known.

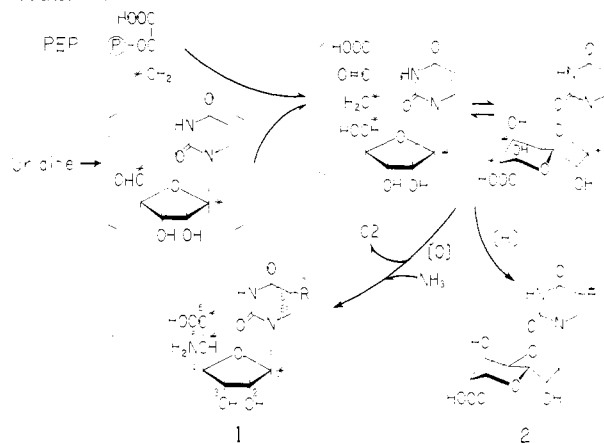


Table I. ^{13}C NMR^a Chemical Shift Assignment and Enrichment of Carbons of Polyoxin C (**1**) Labeled by $[1-^{13}\text{C}]$ Glucose

Carbon atom	Chemical shift, ^b ppm	Relative enrichment ^c
2	152.1	1.40 ^d
4	165.4	0.94
5	114.6	0.90
6	140.9	1.05
7	57.2	1.00
1'	92.2	2.81
2'	73.1	1.23
3'	69.8	0.90
4'	81.5	1.00
5'	54.4	2.81
6'	169.2	3.23

^a ^{13}C NMR spectra were taken on a JOEL FX-60 spectrometer. Solvent: D_2O -1 N HCl (1:1). ^b Chemical shift was expressed in parts per million relative to tetramethylsilane, calculated from dioxane, 67.4. ^c Relative enrichment was obtained by comparison of the integral curves of enriched and unenriched samples under the identical conditions. ^d This enrichment may be explained by the incorporation of $[^{13}\text{C}]$ carbamoyl phosphate which is formed from D- $[1-^{13}\text{C}]$ glucose through the hexose monophosphate oxidative pathway.

volves the condensation of uridine with phosphoenolpyruvate to afford octofuranuloseuronic acid as the intermediate. Subsequent oxidative elimination of the two terminal carbons would form the carbon skeleton of the nucleoside skeleton of the polyoxins (compound **1**, Scheme I).

D- $[1-^{13}\text{C}]$ Glucose⁷ (1.5 g, 90 at. %) was administered to a shaking culture of *Streptomyces cacaoi* var. *asoensis* 72 h after inoculation⁸ (1.2 L of the medium in 20 500-mL flasks; medium composition, 3% glycerol⁹, 1% glucose, 2% soybean meal; 4% dry yeast, 0.2% NaNO_3 , 0.2% K_2HPO_4). After an additional 24-h incubation, the polyoxin complex was isolated from the culture filtrate.¹⁰ Alkaline hydrolysis² of the complex afforded 10 mg of polyoxin C (**1**, R = CH_2OH). The ^{13}C NMR spectrum¹¹ of **1** showed significant enrichment of C-1', C-5', and C-6' (Table I). The distribution of the label clearly indicates that this hexose derivative does not originate from the carbon skeleton of glucose nor is it formed by the condensation of two three-carbon units as suggested earlier.^{3a} Instead, equal enrichment of C-1' and C-5' indicates that C-1' \sim C-5' originates from the ribose carbon skeleton. Known sugar metabolism supports the formation of $[1,5-^{13}\text{C}]$ ribose from $[1-^{13}\text{C}]$ glucose via the pentose phosphate cycle.^{12,13} Taking into account the structure of octosyl acid¹⁴ (**2**, R = COOH or CH_2OH), also produced by *S. cacaoi*, we considered the pos-