leaves little doubt that the acylated phenylisoserine side chain of these taxoids is synthesized via path a of Scheme I. Unexpectedly, in both experiments **1**, but not **2**, also showed a pronounced M + 10 peak, as well as a P + 10 satellite for the m/z 286 fragment representing the side chain. Hence, the aromatic ring of **4a** and **5a** must have also been incorporated into the benzoyl group of the **1** side chain. Together with the non-incorporation of **7a** this suggests the operation of a new pathway, other than the established[13] path b/c of Scheme I, for the genesis of the benzoate moieties in this plant which proceeds from **3** via **4** (path a/d) or **4** and **5** (path a/e).

In summary, the side chain of **1** and **2** is formed from phenylalanine via β-phenylalanine, presumably generated by an aminomutase reaction,[14] followed by hydroxylation of C-2 and acylation of the nitrogen. The benzoyl moiety is also formed via β-phenylalanine and possibly phenylisoserine rather than via cinnamic acid.

Supplementary Material Available: ES–MS spectra of **1** derived from **3a–6a** and of **2** derived from **3a–5a** and standard ES–MS spectra of **1** and **2** (11 pages). Ordering information is given on any current masthead page.

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The Chemical Nature of Amavadin

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Vanadium is an essential trace element.[1,2] Mushrooms of the genus *Amanita* accumulate vanadium ≤200 ppm[3] wherein vanadium forms the 1:2 complex, Amavadin,[4] with (S,S)-2,2'-(hydroxyimino)dipropionic acid, HON{CH(Me)CO₂H}₂ (HIDPAH₃).[5,6] EPR shows that V^{IV} is present[4,5,7–10] which is reversibly oxidizable to V^V.[11] Initially, a VO^{2+} center was postulated,[5,6] but this is no longer favored. An octacoordinated V^{4+} complex with two HIDPA^{3-} ligands, each bonded via a η^2-N,O group and two unidentate carboxylato groups—as in [NH₄][NMe₄][V-(HIDA)₂] (HIDAH₃ = 2,2'-(hydroxyimino)diacetic acid

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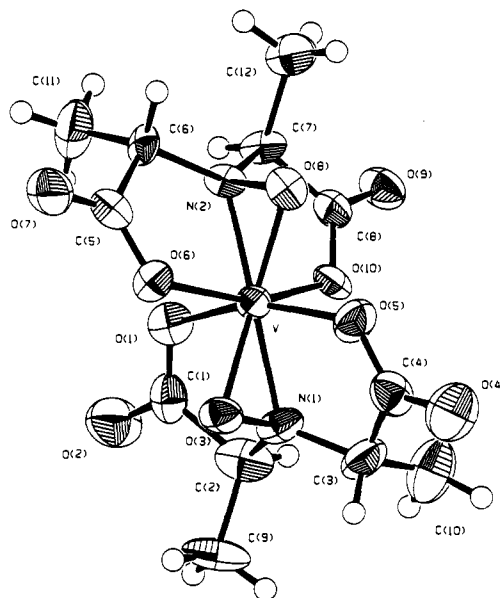(11) Nawi, M. A.; Riechel, T. L. *Inorg. Chim. Acta* **1987**, *136*, 33.

Figure 1. Structure of the anion of [PPh₄][Δ-V((S,S)-HIDPA)₂]·H₂O.

Table I. Comparison of the Vanadium–Ligand Distances^a for [V(HIDA)₂]$^{n-}$ (n = 1, 2) and [Δ-V((S,S)-HIDPA)₂]⁻

bond	length (Å)		
	[V(HIDA)₂]²⁻	[V(HIDA)₂]⁻	[Δ-V((S,S)-HIDPA)₂]⁻
V–O(1)	2.071 (3)	1.991 (7)	1.993 (9)
V–O(5)	2.065 (3)	1.955 (7)	1.96 (1)
V–O(6)	2.063 (3)	1.922 (8)	1.977 (9)
V–O(10)	2.070 (3)	1.936 (7)	1.941 (9)
V–O(3)	1.973 (3)	1.963 (8)	1.926 (9)
V–O(8)	1.976 (3)	1.977 (8)	1.973 (9)
V–N(1)	2.003 (4)	2.016 (8)	2.02 (1)
V–N(2)	2.002 (3)	2.028 (9)	2.00 (1)

^{a} The labeling scheme adopted is defined in Figure 1 for [Δ-V((S,-S)-HIDPA)₂]⁻, and the comparisons are made with respect to the equivalent bonds in [V(HIDA)₂]⁻ and [V(HIDA)₂]²⁻.[14] O(1), O(3), and O(5) belong to the same ligand molecule, and O(3) and O(8) are the hydroxamato O atoms.

(HON{CH₂CO₂H}₂))[12–15]—has been accepted, but not proven, for Amavadin. We have prepared and characterized [Δ-V((S,-S)-HIDPA)₂]⁻, establishing that oxidized Amavadin consists of approximately an equal mixture of the Δ and Λ forms of this anion.

HIDAH₃ and HIDPAH₃ were synthesized (see ref 16a), the latter from L(or D)-alanine via D(or L)-bromopropionic acid.[16b] The acid forms of the V^{IV} complexes were prepared from [VO-(pentane-2,4-dionate)₂] in H₂O, with chromatographic separation on a Dowex column and evaporation to dryness. The V^{IV} complexes were oxidized by [NH₄]₂[Ce(NO₃)₆], and the V^V anion was precipitated with [PPh₄]⁺. Red, prismatic crystals[17,18] of

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[PPh$_4$][V(HIDA)$_2$]·CH$_2$Cl$_2$ and [PPh$_4$][Δ-V((S,S)-HID-PA)$_2$]·H$_2$O were obtained by crystallization from CH$_2$Cl$_2$ and H$_2$O, respectively. The structures of these and related[19] anions correspond closely to that of their V^{IV} counterpart in [NH$_4$]-[NMe$_4$][V(HIDA)$_2$].[14] Figure 1 shows the geometry of [Δ-V-((S,S)-HIDPA)$_2$]$^-$; the stereochemistry at the metal is designated Δ by considering the relative positions of the two VON triangles as viewed perpendicular to the VO$_4$ plane. Overall, both complexes possess idealized C_2 symmetry. The vanadium–ligand distances for [V(HIDA)$_2$]$^{n-}$ (n = 1, 2) and [Δ-V((S,S)-HIDPA)$_2$]$^-$ (Table I) show that oxidation results in a significant contraction of one V–O(6) bond and a modest contraction of three V–O$_{carboxylate}$ bonds, but no significant change in the V–O,N$_{hydroxyimino}$ distances. Thus, the SOMO of the V^{IV} systems is located in the VO$_4$ plane.

XAS have been recorded for *Amanita muscaria* and several of its chemical relatives.[20] The general lack of a pre-edge feature contrasts with observations for systems containing one (or more) V=O groups.[22–24] The EXAFS of the synthetic systems is well interpreted by back-scattering from 6 O, 2 N, 8 C, and 4 O atoms at the crystallographic distances with inclusion of multiple scattering for the outer shell. The EXAFS for V^{IV} Amavadin is simulated successfully by back-scattering from 6 oxygens at 2.01 Å, 2 nitrogens at 2.04 Å, 8 carbons at 2.94 Å, and 4 oxygens at 4.0 Å with no indication of a short V=O contribution.

Cyclic voltammetry of Amavadin and its chemical analogues (refs 11 and 13, and this work) indicates that each of the V^{IV}/V^V pairs possesses a common geometry in solution. [V(HIDA)$_2$]$^-$ manifests ^{1}H and ^{13}C NMR spectra consistent with retention of the molecular geometry in solution; the ^{51}V resonance is at −263 ppm vs VOCl$_3$. The ^{1}H and ^{13}C NMR spectra of [Δ-V((S,S)-HIDPA)$_2$]$^-$ are consistent with the structure (Figure 1) persisting in solution, and the ^{51}V resonance is at −281 ppm. The ^{1}H NMR spectrum of oxidized Amavadin displays four doublets in the methyl region coupled to four quartets in the methine region; the relative integrals within these sets are approximately equal. Analogous sets of four resonances are seen in the ^{13}C NMR spectrum and a single ^{51}V resonance is observed at −280 ppm. The two doublets and two quartets seen in the ^{1}H NMR spectrum of [Δ-V((S,S)-HIDPA)$_2$]$^-$, and the sets of two resonances seen in the ^{13}C NMR spectrum, can be overlaid with half of the corresponding features of oxidized Amavadin. Therefore, oxidized Amavadin possesses two ligands with the same stereochemistry coordinated to the vanadium as in [V(HIDA)$_2$]$^{n-}$ (n = 1, 2) and [V((S,S)-HIDPA)$_2$]$^-$, but consists of an approximately equal mixture of the Δ and Λ forms of [V((S,S)-HIDPA)$_2$]$^-$.

This conclusion is consistent with optical spectra. Oxidized and reduced Amavadin each manifest an electronic absorption spectrum which is essentially the same as the equivalent spectrum from

an HIDPA complex. However, the CD spectra of the oxidized and reduced forms of Amavadin have profoundly different sign distributions from those of the corresponding state of [Δ-V-(HIDPA)$_2$]$^{n-}$ (n = 1, 2). Furthermore, a CD spectrum identical to that of reduced Amavadin can be obtained by reducing [Δ-V((S,S)-HIDPA)$_2$]$^-$ with Na$_2$S$_2$O$_4$ and allowing the solution to stand for several hours. Reoxidation with [NH$_4$]$_2$[Ce(NO$_3$)$_6$] produces CD and ^{1}H and ^{13}C NMR spectra identical to those of oxidized Amavadin. Thus, [Δ-V((S,S)-HIDPA)$_2$]$^{2-}$ racemizes at the V^{IV} center.

These studies not only establish the chemical nature of Amavadin but also demonstrate that this species belongs to the group of transition metal centers in biology (e.g., blue copper, cyctochromes, iron–sulfur) which retain their structure through a one-electron redox change.

Kinetic, Spectroscopic, and Structural Evidence for Carbene–Carbyne Intermediates in Carbyne/CO Coupling

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Understanding the intimate mechanism of carbon–carbon bond formation between two ligands in an organometallic complex is of fundamental interest. Coupling of carbyne and CO or CNR ligands has become a general class of such reactions.[1–5] Both η^2-ketenyl and carbene–carbyne intermediates have been shown or postulated to be involved in the key C–C bond forming step.[6–9] Recently we demonstrated that the reductive coupling of CO ligands in [M(CO)$_2$(dmpe)$_2$Cl] (M = V, Nb, or Ta) to form [M(R$_3$SiOC≡COSiR$_3$)(dmpe)$_2$X] occurs via sequential formation of Na[M(CO)$_2$(dmpe)$_2$] and [M(≡COSiR$_3$)(CO)(dmpe)$_2$] complexes.[9–11] In order to elucidate further details of the coupling step, we have undertaken the first kinetic study of carbyne/CO coupling. Here we report that the rate-determining step of the reaction of [Ta(≡COSi^{i}Pr$_3$)(CO)(dmpe)$_2$] (1) with Me$_3$SiCl to form [Ta(^{i}Pr$_3$SiOC≡COSiMe$_3$)(dmpe)$_2$Cl] (2)[9] involves electrophilic attack by the silyl reagent upon the terminal CO ligand

(18) [PPh$_4$][Δ-V((S,S)-HIDPA)$_2$]·H$_2$O crystallizes in the orthorhombic space group $P2_12_12_1$; a = 1530 (1), b = 2818 (2), c = 854.6 (5) pm, V = 3685 (4) × 10^6 pm^3, Z = 4; F(000) = 1576, ρ_{calcd} = 1.363 g cm^{-3}; μ = 3.60 cm^{-1}; Mo Kα radiation, $2\theta_{max}$ = 39.9°; 2107 reflections measured, 1837 observed ($I > 3\sigma I$); number of parameters 460; R = 0.068, R_w = 0.093.

(19) The crystal structures of [PPh$_4$][V((R,S)-HIDPA)$_2$]·CH$_2$Cl$_2$ and [PPh$_4$][V((R,S)-HIDPA)((S,S)-HIDPA)]·CH$_2$Cl$_2$ have also been determined. These anions possess a set of bond lengths similar to those detailed for the vanadium(V) complexes in Table I.

(20) Vanadium K-edge X-ray absorption spectra (XAS) were recorded on stations 7.1 and 8.1 of the Daresbury Synchrotron Radiation Source for *Amanita muscaria* extract (ex. Sigma), an aqueous solution of Amavadin in its V^{IV} state, a CH$_2$Cl$_2$ solution of Amavadin oxidized by treatment with [NH$_4$]$_2$[Ce(NO$_3$)$_6$], and solid samples of [NH$_4$][NMe$_4$][V(HIDA)$_2$], H$_2$[V-((R,S)-HIDPA)$_2$], [PPh$_4$][V(HIDA)$_2$]·CH$_2$Cl$_2$, and [PPh$_4$][V((R,S)-HID-PA)$_2$]·CH$_2$Cl$_2$. The energy of the vanadium K-edge[21] was found to be 5480.8 and 5482.4 ± 0.3 eV for the vanadium(IV) and -(V) centers, respectively, consistent with the variation expected[22–24] between these oxidation states, although the values are slightly higher than the corresponding edge positions of oxovanadium(IV) and -(V) compounds.

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