duction of $[Os(NH_3)_5(DME)]^{3+}$. This is in contrast to the electrochemical behavior of $[Os(NH_3)_5(ethylene)]^{2+}$, which shows reversible electrochemistry at scan rates as low as 50 mV/s.[13] The cyclic voltammogram of **2** shows two oxidation waves at +0.35 and +0.85 V (NHE). Upon return scan there is a single wave at −0.75 V (NHE), indicating dissociation of the fully oxidized species. In contrast, if the switching potential is reset to +0.5 V, so that the potential remains negative of the second oxidation wave, the first oxidation at +0.35 V becomes reversible (see Figure 3), which shows that the mixed-valence complex is stable at least on the electrochemical time scale.

Figure 4 shows the near-IR absorption spectrum of a solution of **2** in neat acetone-d_6, with 1 equiv of $[FeCp_2]PF_6$ added and with 2 equiv of $[FeCp_2]PF_6$ added. The spectrum of the mixed-valence complex $[(Os(NH_3)_5)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-benzene})]^{5+}$ features a broad asymmetric absorption at 1750 nm (ϵ 220) with a width at half-maximum of 1600 cm^{-1}. Though this band is rather weak, its width is less than half of that calculated by the Hush model for a valence trapped system.[14] This feature along with the large separation in potential of the first and second oxidation waves suggests that $[(Os(NH_3)_5)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-benzene})]^{5+}$ is a fully delocalized class III mixed-valence complex.[15] Additional features at 2140 and 2460 nm are presumed to be spin-orbit transitions arising from the unpaired electron. The positions of these peaks, compared to those of typical Os(III) mononuclear complexes, are further indication of the delocalization in the binuclear complex.[16]

The high affinity of pentaammineosmium(II) for unsaturated ligands has been demonstrated in the case of dinitrogen,[17] ketones,[1] aldehydes,[18] and now aromatic hydrocarbons. In addition pentaammineosmium(II) appears to exhibit unusual reactivity toward both amides and esters. Our future efforts will be focused on the further development of this chemistry.

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Biosynthesis of Sesbanine. A Novel Origin for the Carbon Skeleton

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In 1979, Powell and co-workers isolated the unique alkaloid sesbanine (**1**) from cytotoxic seed extracts of *Sesbania drummondii* (Leguminosae).[1] Sesbanine initially appeared to exhibit marked inhibition in the P388 leukemia screen, but later studies showed that the highly purified compound is inactive.[1] The activity of *Sesbania* extracts was eventually traced to the presence of a structurally unrelated substance called sesbanamide.[2] Although sesbanine lacks apparent biological activity, the alkaloid still excites interest because of its unprecedented structure. This fact prompted us to pursue the biosynthetic investigations of sesbanine that will now be described.

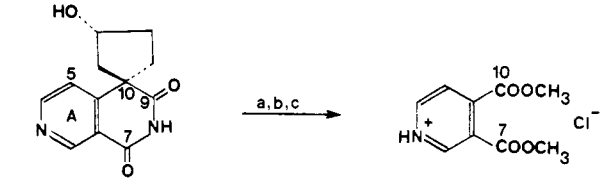
The extremely low concentrations of sesbanine in *S. drummondii* seeds[1] made it necessary to carry out biosynthetic studies using isotope dilution methods. The sesbanine required as carrier was obtained via total synthesis.[3] The structure of sesbanine suggested that nicotinic acid might be a specific precursor. Accordingly, preliminary experiments were carried with [carboxyl-^{14}C]nicotinic acid to optimize conditions for precursor incorporations. The best conditions gave an incorporation of 0.002% with this substance (Table I, experiment 1). The sesbanin biosynthesized from [*carboxyl*-^{14}C]nicotinic acid in experiment 1 was degraded (Scheme I) to dimethyl pyridine-3,4-dicarboxylate hydrochloride (**2**), which carried 68% of the total radioactivity (theory = 100%). The low incorporation and relatively low specificity observed with nicotinic acid suggested that the plants may not efficiently utilize administered nicotinic acid. Therefore, tryptophan, which is a known nicotinic acid precursor in animals and some microorganisms,[4] was evaluated as a sesbanine precursor. Administration of [5-^{3}H]tryptophan to *Sesbania* was followed by workup with dilution for both sesbanine and nicotinic acid. The results of this experiment (Table I, experiment 2) were gratifying, since good incorporations into both substances were obtained. Furthermore, the tritium label in the isolated sesbanine and

Table I. Administration of Labeled Precursors to *S. drummondii*[a]

expt	precursor	% incorpn	labeling pattern
1	[*carboxyl*-^{14}C]-nicotinic acid	0.002	68% in diester hydrochloride **2**
2	[5-^{3}H]-L-tryptophan	0.02 (sesbanine)	90% at C-5
		0.11 (nicotinic acid)	100% at C-5
3	[U-^{14}C]-L-tyrosine	0.002	
4	[U-^{14}C]-L-phenylalanine	0.007	
5	[G-^{14}C]shikimic acid	0.025	17% in diester hydrochloride **2**
6	[7-^{14}C]shikimic acid	0.042	90% at C-9
7	[U-^{14}C]-*p*-hydroxybenzoic acid	0.082	18% in diester hydrochloride **2**, 97% in oxindole **3**, 79% in phthalimidine **4**

[a] All precursors were administered to 6-week-old *Sesbania* plants by the cotton-wick method for a 7-day period.

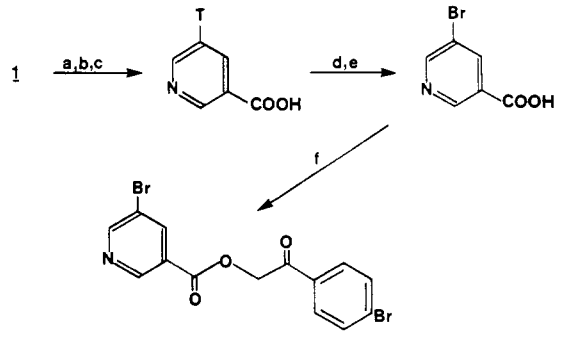
Scheme I



1 2

[a] $KMnO_4$, KOH. [b] CH_2N_2. [c] HCl.

Scheme II



[a] PhCOCl, C_5H_5N. [b] $KMnO_4$, KOH. [c] Δ. [d] $SOCl_2$. [e] Br_2. [f] *p*-$BrPhCOCH_2Br$, K_2CO_3, crown ether.

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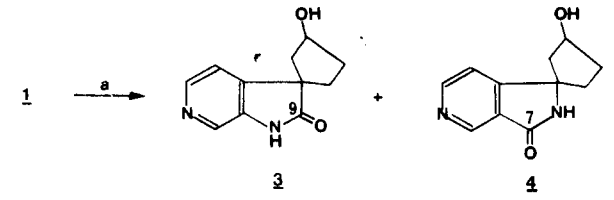
Scheme III



[a] NaClO, NaOH.

nicotinic acid was shown to reside entirely at the expected position[4] (C-5) by the degradation outlined in Scheme II. These findings demonstrate that nicotinic acid is biosynthesized from tryptophan in *Sesbania* and that nicotinic acid is a specific precursor of sesbanine. The observed formation of nicotinic acid from tryptophan is of interest, since the current evidence for the operation of this pathway in higher plants is equivocal.[5,6]

The origin of ring A and C-7 of sesbanine having been established, efforts were focused on elucidation of the origin of the cyclopentane moiety of the alkaloid. The six carbon atoms (C-9 to C-14) were postulated to be derived from an aromatic ring by a ring-contraction process that might be similar to that observed in the *Cephalotaxus* alkaloids.[7] Accordingly, tyrosine, phenylalanine, and shikimic acid were evaluated as precursors (Table I, experiments 3-5). Tyrosine and phenylalanine gave poor incorporations, while shikimate appeared more promising. Degradation (Scheme I) of the sesbanine derived from [G-^{14}C]shikimate disclosed that the pyridine dicarboxylic ester **2** carried 17% of the total radioactivity (theory = 17%). Further proof that shikimic acid is a specific precursor of sesbanine was obtained by administration of [7-^{14}C]shikimate[8] to *Sesbania*. Degradation of the labeled sesbanine obtained in this experiment (Table I, experiment 6) by the route shown in Scheme III revealed that 90% of the radioactivity was present in the oxindole **3**, while the phthalimidine **4** was inactive. Shikimate therefore appears to be a specific precursor of the cyclopentanoid moiety of sesbanine. Additional information on the mode of incorporation of shikimate was provided by evaluation of *p*-hydroxybenzoic acid, which is known to be derived from chorismic acid in bacteria.[9] Administration of [U-^{14}C]-*p*-hydroxybenzoate to *Sesbania* gave the highest incorporation figure yet observed for a sesbanine precursor (Table I, experiment 7), and degradations proved the incorporation to be specific. Degradation of the sesbanine according to Scheme I yielded diester hydrochloride **2** that carried 18% of the total activity (theory = 17%), while degradation according to Scheme III yielded oxindole **3** bearing 97% of the radioactivity (theory = 100%) and phthalimidine **4** bearing 79% of the radioactivity (theory = 83%).

In summary, our investigations show that sesbanine is biosynthesized from nicotinic acid and *p*-hydroxybenzoic acid with loss of one carbon atom from the aromatic ring of the latter compound. The intermediate stages of this novel biosynthetic pathway remain to be elucidated.

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Control of Bulk Dipolar Alignment Using Guest-Host Inclusion Chemistry: New Materials for Second-Harmonic Generation

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Second harmonic generation (SHG) is a subset of nonlinear optical properties which is currently under intensive investigation at laboratories around the world.[1] Many polar, acentric organic and inorganic materials are capable of efficient SHG when subjected to intense optical fields encountered under laser irradiation. From a physical organic perspective, it is useful to consider the electronic properties of those materials that have proved to be effective for SHG. Oudar[2] has suggested that a simple two-level model is adequate for predictive use in a search for new materials. Within this framework, polar materials which possess low-lying charge-transfer states, or which experience large changes in molecular dipole moment on photoexcitation, are potential SHG active materials. These are materials that are anticipated to have high molecular second-order polarizability, β, which will contribute to the field-induced dipole moment, μ (eq 1). Physical organic

$$\mu = \mu_0 + \alpha\mathbf{E} + \beta\mathbf{EE} + \gamma\mathbf{EEE} + \ldots \quad (1)$$

and organometallic chemists can list many small molecules which may be SHG active based on this simple criterion. Unfortunately, many inherently interesting molecules fail to be SHG active in the bulk because their crystal space group is centrosymmetric, and the bulk polarizability of the material vanishes because of symmetry restrictions on the expansion of the bulk polarization **P**, a vectoral quantity (eq 2). To date, methods for engineering

$$\mathbf{P} = \mathbf{P}_0 + \chi^{(1)}\mathbf{E} + \chi^{(2)}\mathbf{EE} + \chi^{(3)}\mathbf{EEE} + \ldots \quad (2)$$

small polar molecules into acentric environments have been restricted to thin film (Langmuir-Blodgett monolayers,[3] orientation of molecules in polymer glasses[4] using strong electric or magnetic fields, or use of liquid-crystalline mesogens[4]) or directed crystal growth techniques.[5] We now report that polarizable materials whose natural crystal habit may be centrosymmetric (thus incapable of SHG) can be induced to exhibit SHG by inclusion into a host lattice structure[6] which imparts a polar director to the alignment of the molecular dipoles. The use of inclusion compound hosts appears, surprisingly, to be a general method for dipolar alignment of organic and organometallic compounds.[7]

We have found that inclusion hosts such as thiourea, tris(*o*-thymotide) (TOT), and deoxycholic acid, as well as clathrate hosts such as cyclodextrins[7] (CD), are capable of forming polar

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