parameters are plotted vs. Z in Figure 1 and tabulated in Table I. It is obvious that these parameters vary smoothly as a function of Z, thereby allowing the intermediate elements to be interpolated. Two important chemical trends readily emerge: the inverse of the width (B) generally decreases whereas the peak position (C) generally increases with increasing atomic number Z. It is apparent that these two slowly varying parameters (as a function of Z) can be used for chemical identification in complex or unknown systems. Examples include the differentiation of metal-metal from metal-ligand (lighter atom) bonds in polymer,[15] biological,[16] or metal cluster[17] systems. Due to effects not accounted for in the theory,[8b] parameter A requires an additional scale factor in the fitting of the EXAFS spectra.[13b] However, in cases involving direct bonding it is possible to use the relative values of A to infer the relative number of neighboring atoms (coordination numbers, N_j) and hence to differentiate plausible structures.[15-17] Another important utility of these theoretical parameters is the estimation of Debye-Waller factors which is difficult, if not impossible, to extract from experimental EXAFS data alone (vide supra).[20]

Using these amplitude parameters, along with the parameterized theoretical phase shifts,[21] we have fitted a number of known systems. Figures 2a and b show the least-squares fit (dashed curves) to the EXAFS (full curves) spectra of Br_2 and $GeCl_4$, respectively.[4a,10] It is evident that the agreements between theoretical and experimental amplitudes (vide supra) are fairly good. Experimentally, the $\chi(k)k^3$ data peak at ca. 10.9 and 7.1 $Å^{-1}$ in Br_2 and $GeCl_4$, respectively. In the absence of Debye-Waller factor, our amplitude function multiplied by k^2 (viz., $F(k)k^2$) peaks at 13.1 and 8.5 $Å^{-1}$ for scatterer Br and Cl, respectively.[18] A Debye-Waller factor of 0.050 (6) Å in Br_2 and 0.043 (6) Å in $GeCl_4$ is found by least-squares refinement to lower the peak position to the observed values (cf. Figure 2). These are in good agreement with the reported value of 0.045 Å for both compounds.[4a,19b]

Finally, it should be emphasized that amplitude functions (and hence our parameters A, B, and C) depend upon the backscatterer only, unlike phase shifts which depend on both the absorber and the backscatterer. We believe the transferability of amplitude functions can be used to provide valuable chemical (coordination numbers and Debye-Waller factors) as well as structural (interatomic distances) information in EXAFS spectroscopy.[20]

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(11) Equation 1 derives from a single scattering theory[1,6] for excitation of an s state. The photoelectron wave vector $k = ((2m/\hbar^2)(E - E_0))^{1/2}$ where E is the photon energy and E_0 is the threshold.
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(13) (a) The EXAFS spectra were "approximately" normalized with Victoreen's true absorption coefficient $\mu_0/\rho = C\lambda^3 - D\lambda^4$ ("International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1968, pp 161, 171). This partly explains why A is not in as good agreement as B and C. (b) The theoretical A value, which includes inelastic processes in the scattering atom is found to be off by ~50%. Part of this discrepancy is due to core relaxation effects.[8b] Furthermore, the absolute value of A is expected to be somewhat sensitive to the chemical environment and will depend on the distance r_i (an exponential damping factor $e^{-2\gamma r_i}$ is usually added to eq 1). An overall scale factor (e.g., 0.66 in Br_2 and 0.41 in $GeCl_4$) is therefore included in the refinements.
(14) (a) To compensate for amplitude reduction, the actual theoretical amplitude functions were multiplied by k^2 and then fitted with $F(k)k^2 = Ak^2/(1 + B^2(k - C)^2)$. This procedure corresponds to fitting the experimental $\chi(k)k^3$ data with both sides of eq 1 multiplied by k^3. (b) We note that the theory is less reliable for energy below 60 eV ($k \lesssim 4$ $Å^{-1}$) due to the inadequate treatment of valence electrons. This problem is particularly serious for light atoms ($Z < 9$) where the peak at $k \lesssim 2$ $Å^{-1}$ should be treated with caution.
(15) J. Reed, P. Eisenberger, B. K. Teo, and B. M. Kincaid, submitted for publication.
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(18) Note that $F(k) = A/(1 + B^2(k - C)^2)$ peaks at C whereas $F(k)k^2 = Ak^2/(1 + B^2(k - C)^2)$ peaks at $C + 1/(B^2C)$.
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(21) P. A. Lee, B. K. Teo, and A. L. Simons, *J. Am. Chem. Soc.*, following paper in this issue.

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EXAFS: a New Parameterization of Phase Shifts[1]

Sir:

Extended x-ray absorption fine structure (EXAFS) spectroscopy has become an important structural tool for complex systems in recent years.[2-10] There are two major approaches in data analysis: the Fourier transform[2,3,9] and the least-squares fitting[4-6] techniques. Both of these methods require a detailed knowledge of the phase function[2,5] $\phi(k)$ (cf. eq 1 of preceding article). If we have an absorbing atom A and a backscattering atom B, the phase function ϕ_{ab} is given by

$$\phi_{ab}(k) = \phi_a(k) + \phi_b(k) - \pi \qquad (1)$$

where $\phi_a = 2\delta_1'$ is the $l = 1$ (for K and L_I edges) phase shift of the central atom and ϕ_b is the phase of the backscattering amplitude.[9] The factor of π is required (as a matter of convention) to make the amplitude function $F(k)$ positive. Citrin, Eisenberger, and Kincaid[5] have parameterized experimental phase shifts by a quadratic function in k. They also demonstrated that phase shifts are transferable from one chemical system to another, thereby enabling accurate determination of interatomic distances in unknown systems based on known distances of model compounds.[5] Unlike the backscattering amplitude[1] which is a function of the scatterer[9] only, the phase shift depends upon both the absorber (central atom) and the backscatterer (neighboring atom).[9] Thus, while phase shifts can be deduced empirically from model compounds with known distances,[2,5] it is only possible to determine the combination $\phi_{ab}(k)$ for each atom-pair A-B and not the two contributions ϕ_a and ϕ_b separately. To avoid the trouble of searching for model compounds in each EXAFS problem, it

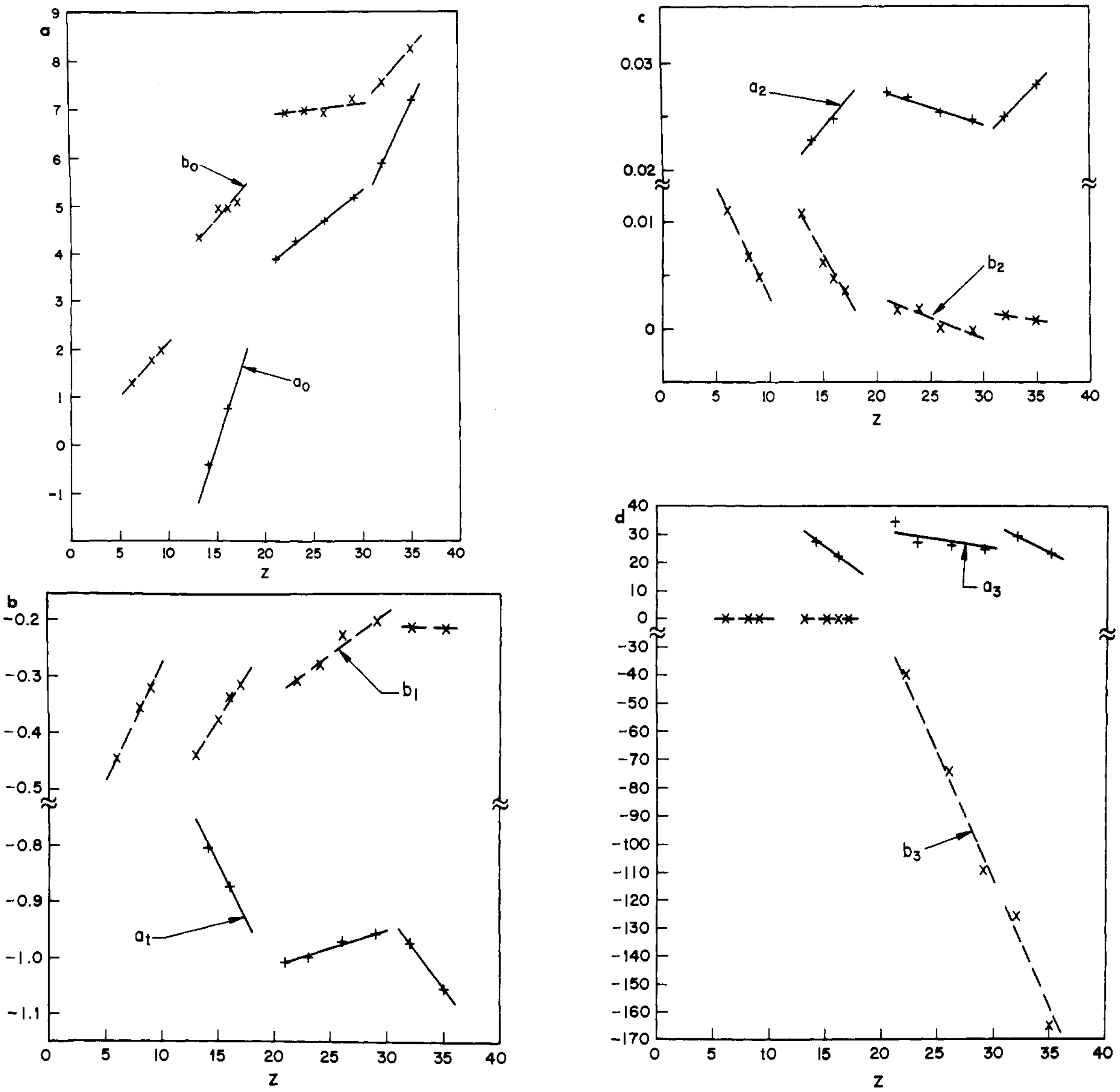

Figure 1. Absorber (solid) and backscatter (dashed) phase parameters (a_i and b_i) vs. atomic number Z: (a) a_0, b_0; (b) a_1, b_1; (c) a_2, b_2; (d) a_3, b_3.

is clearly desirable to calculate,[7-10] parameterize, and tabulate ϕ_a and ϕ_b individually from theory which can then be combined to give ϕ_{ab}. We report here the parameterization of theoretical phase shifts[9] via a new functional form and the application of a least-squares fitting technique using these as well as the amplitude[1] parameters to determine interatomic distances (accurate to ca. 0.01 Å) in a number of known systems.

Recently Lee and Beni[9] have presented a new electron atom scattering theory and applied their methods to EXAFS for a few combinations of atomic pairs. We have used their method to generate phase shift functions for elements with atomic number Z = 6-35.[11] While ϕ_a can be approximated by a quadratic function,[5] the calculated ϕ_b cannot be adequately described by this function due to the existence of a broad maximum in the calculated curve which moves to higher k as Z increases.[9] Subsequently we find that both ϕ_a and ϕ_b can be fitted adequately with

$$\phi_a(k) = a_0 + a_1 k + a_2 k^2 + a_3/k^3 \tag{2}$$

and

$$\phi_b(k) = b_0 + b_1 k + b_2 k^2 + b_3/k^3 \tag{3}$$
$$4 \lesssim k \lesssim 16\ \text{Å}^{-1}$$

where

$$k = \left[\frac{2m}{\hbar^2}(E - E_0)\right]^{1/2} \tag{4}$$

is the photoelectron wave vector in Å^{-1}. The parameter E_0 denotes the energy threshold. Table I tabulates the least-squares refined parameters for 8 absorber and 13 backscatterer phase shifts.[13] Since the fitting of the theoretical curves with eq 2 and 3 was done over the range of 4-16 Å^{-1}, our parameterized functions should not be used outside this range. It should also be pointed out that the k^{-3} term is introduced here to better fit the theoretical ϕ_b for $Z < 36$ and that there is no experimental evidence indicating that this form is to be preferred over the quadratic function. Figures 1a-d depict the variation of these parameters as a function of atomic number Z. It is clear that these parameters exhibit smooth trends of chemical significance. In particular, each parameter follows essentially linear behavior within each series (2p, 3p, 3d, etc.), thereby allowing the intermediate elements to be interpolated. Abrupt changes occur upon completion of a shell primarily due to the drastic change in atomic radius and electronic configuration. We have excluded alkali and alkali earth metals in the present parameterization since it will be more appropriate to treat these elements as ions and hence there is no a priori reason to believe that they will fit smoothly in the present scheme. A few trends are apparent in Figure 1. First, within each shell,

Table I. The Fitted Theoretical Backscatterer and Absorber Phase Parameters for Elements with Atomic Number $Z = 6$–35

		Back-scatterer				Absorber			
Z	Chem	b_0	b_1	b_2	b_3	a_0	a_1	a_2	a_3
6	C	1.279	−0.4452	0.01113	0				
8	O	1.675	−0.3542	0.00675	0				
9	F	1.955	−0.3199	0.00494	0				
13	Al	4.321	−0.4393	0.01078	0				
14	Si					−0.414	−0.8040	0.02270	27.77
15	P	4.919	−0.3743	0.00619	0				
16	S	4.940	−0.3368	0.00480	0	0.756	−0.8731	0.02471	22.40
17	Cl	5.091	−0.3116	0.00373	0				
21	Sc					3.875	−1.0096	0.02722	34.65
22	Ti	6.915	−0.3054	0.00174	−39.57				
23	V					4.216	−1.0000	0.02674	27.51
24	Cr	6.977	−0.2789	0.00184	−66.02				
26	Fc	6.912	−0.2225	0.00001	−73.99	4.682	−0.9706	0.02521	26.64
29	Cu	7.206	−0.2000	−0.00010	−109.62	5.148	−0.9586	0.02459	25.21
32	Ge	7.553	−0.2103	0.00124	−126.45	5.902	−0.9731	0.02479	29.41
35	Br	8.268	−0.2117	0.00087	−165.17	7.194	−1.0554	0.02792	23.54

both a_0 and b_0 increase linearly with Z as a result of the increasingly attractive potential.[9] Second, we observe that both a_1 and b_1 are negative. A comparison of a_1 with b_1 also reveals, as expected, that the central atom phase ϕ_a has a stronger k dependence (i.e., $|a_1| > |b_1|$) than the backscatterer phase ϕ_b. Finally, b_3 becomes more negative with increasing Z due to a broad maximum in ϕ_b which moves to higher k as Z increases.[9]

With these parameters, the total phase function ϕ_{ab} of each pair of atoms AB can be obtained by taking simple sums of the corresponding parameters in ϕ_a and ϕ_b:

$$\phi_{ab}(k) = (a_0 + b_0 - \pi) + (a_1 + b_1)k + (a_2 + b_2)k^2 + (a_3 + b_3)/k^3 \quad (5)$$

We have calculated a variety of phase shift functions. These are applied, along with the parameterized theoretical amplitude functions,[1] to a number of known systems via least-squares refinement technique. Four parameters are varied here: the overall magnitude, the Debye–Waller factor σ, the distance r, and E_0 (cf. eq 4). The agreements between theory and experiment are generally of the same high quality as shown in Figure 2 in the preceding paper.[1] Table II (supplementary material) summarizes the resulting interatomic distances.[14] (See paragraph at end of paper regarding supplementary material.) In single-shell systems, the accuracy is $\lesssim 0.01$ Å, well within the fitting error of $\lesssim 0.015$ Å.[15]

Two points need to be addressed here. First, phase shifts are unique only if E_0 is specified.[9] Changing E_0 by $\Delta E_0 = E_0' - E_0$ will change k to $k' = (k^2 - 2(\Delta E_0)/7.62)^{1/2}$ where k is in Å^{-1} and ΔE_0 in eV. To fit experimental data based upon some experimental E_0 with theoretical phase shifts, we must allow E_0 to vary. It has been shown[9] that by adjusting E_0 it is not possible to produce an artificially good fit with a wrong distance r' simply because changing E_0 will affect $\phi(k)$ (mainly at low k values) by $\sim 2r(\Delta E_0)/(7.62k)$ whereas changing r will affect $\phi(k)$ (mostly at high k values) by $2k(\Delta r)$. Secondly, we find that theoretical phase functions (particularly ϕ_a) are somewhat sensitive to electronic configuration (e.g., $4s^2 3d^9$ vs. $4d^1 3d^{10}$ for Cu). However, the difference again decreases as k increases and can largely be compensated by varying E_0.

Finally we should point out that the straight lines drawn in Figure 1 only serve the purpose of indicating the general trends. The phase functions are not very sensitive to variation in the parameters as long as these are varied in a correlated manner. Thus interpolation between two calculated points will give similar results as reading the points from the straight lines even though the individual parameters are slightly different. This is of course not the case if a single parameter is changed at a time (e.g., change in a_1 or b_1 alone will induce a change in distance).

In conclusion, our parameterized theoretical phase shifts and amplitude[1] functions can be used in curve fitting of EXAFS spectra to give interatomic distances accurate to ca. 0.01 Å (for single-shell systems), without resorting to model compounds. Similar procedure has been applied to the analysis of EXAFS spectra of multiatom multidistance systems with an accuracy of $\lesssim 0.03$ Å.[14c–e]

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Supplementary Material Available: Comparison of EXAFS distances (Table II) (1 page). Ordering information is given on any current masthead page.

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(13) For light scatterers with $Z \leq 17$, the b_3 term was found to be relatively small ($\lesssim 30$) and unimportant. It was set equal to zero in order to obtain smooth trends for plots of b_0, b_1, and b_2 vs. Z.
(14) (a) All data were Fourier filtered (after background removal) and corrected for μ_0 via Victoreen's true absorption coefficient equation ($\mu_0/\rho = C\lambda^3 - D\lambda^4$). (b) Data obtained at SLAC–SSRP and kindly supplied by B. M. Kincaid. For these crystalline materials the first shell contribution was isolated using a Fourier filtering procedure developed by B. M. Kincaid. The resulting distances are in agreement with the Fourier transform method.[9]

(c) R. G. Shulman, B. K. Teo, P. Eisenberger, G. S. Brown, and B. M. Kincaid, to be submitted for publication; (d) J. Reed, P. Eisenberger, B. K. Teo, and B. M. Kincaid, submitted for publication; (e) B. K. Teo, P. Eisenberger, and B. M. Kincaid, to be submitted for publication.

(15) The fitting error for each parameter is calculated by changing that particular parameter (while least-squares refined the others) until the chi-square doubled.

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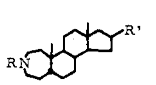
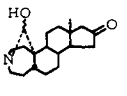
Denial of the Proposed Structure of Salamander Alkaloid, Cycloneosamandaridine. Total Synthesis of Cycloneosamandione and Supposed Cycloneosamandaridine

Sir:

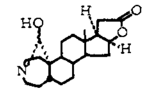
The unique 10-retro-steroidal structure of cycloneosamandione **2**,[1] one of the biologically active salamander alkaloids,[2] proposed by Habermehl and Göttlicher by their x-ray study, has been revised to a normal configuration (**2** → **16**). This interesting revision is a result of their synthetic studies,[3,4] and seems to be supported by our synthesis[5,6] of *N*-acetylsamane **1a** (one of the degradation products).[7] The key step of our synthetic sequence involves a specific Beckmann rearrangement of the geometrically pure isomers of steroidal 3-ketoximes.[5] We have used this method also in the synthesis of the other natural alkaloid, samanine **1b**.[8] The accuracy of this method has been proved by Weiler's independent synthesis of the samanine type alkaloids.[9] However, we have been shaken by Habermehl's comments[10] to the effect that our synthetic specimen was contaminated with a small amount of the regioisomer.



1a, R = Ac; R′ = H
N-acetylsamane
b, R = H; R′ = OH
samanine



2



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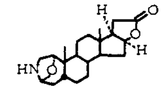
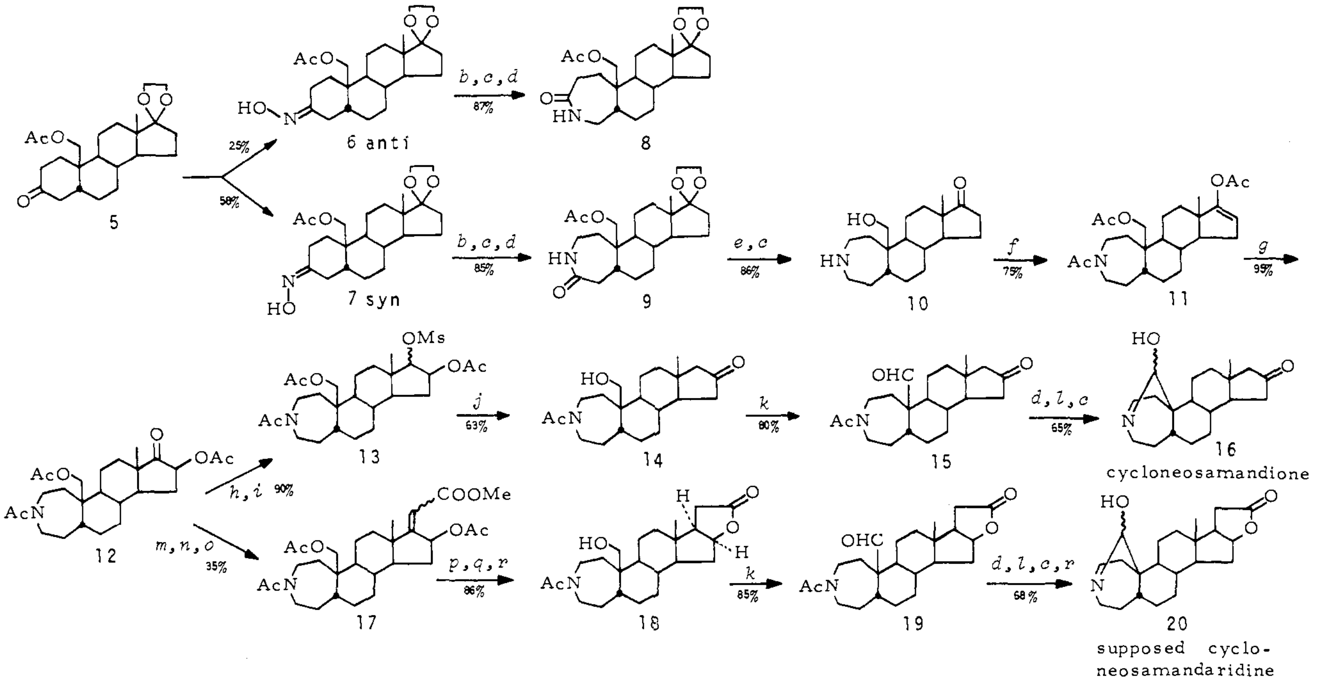


4, samandaridine

We will show in this paper that our method is still an excellent one for the synthesis of 5β-3-aza-A-homo ring system in the salamander alkaloids by the synthesis of cycloneosamandione **16** and cycloneosamandaridine **20**. The main object of the present synthesis is to confirm the structure of cycloneosamandaridine which had been believed to be **3** by Habermehl and Haaf[11] who, at that time, compared its IR and mass spectra[12] with those of cycloneosamandione **2** and samandaridine **4**.[13] Since the structure of cycloneosamandione has been revised (**2** → **16**), it follows that the 10-retro configuration of cycloneosamandaridine must now be revised to a normal one (**3** → **20**). However, the absence of an M − 29(CHO) peak in the mass spectrum of cycloneosamandaridine[11] compelled us to synthesize the supposed structure **20** and compare its mass spectrum with those of the related alkaloids, especially cycloneosamandione **16** where the M − 29 peak is very strong.[1] Our synthetic sequence of these two alkaloids is shown in Scheme I.

The baseline resolution of a mixture of ketoximes prepared from the corresponding ketone **5**[19] into the geometrical isomers was achieved by silica gel column chromatography: anti isomer **6** (less polar, 25%, mp 238–240 °C; δ (pyr-d_5) 3.65 (2β-H)) and the desired syn isomer **7** (more polar, 58%, mp 234–236 °C; δ (pyr-d_5) 3.50 (4β-H)). The assignment of these isomers was based on the NMR of each isomer.[20] For the large scale

Scheme I



[a] $NH_2OH \cdot HCl$, pyr, room temp. [b] TsCl, pyr, 37 °C, 3 h. [c] Dilute HCl, room temperature. [d] Ethylene glycol, TsOH (trace), C_6H_6, reflux. [e] LAH, Et_2O–THF, reflux, 3 h. [f] Isopropenyl acetate, H_2SO_4 (trace), reflux, 7 h. [g] $Pb(OAc)_4$, HOAc, Ac_2O (trace), room temp. over night. [h] $NaBH_4$, MeOH, room temp. [i] MsCl, pyr, room temp. [j] KOH, 95% EtOH, reflux, 1.5 h. [k] CrO_3, H_2SO_4, 0 °C. [l] KOH, *n*-BuOH, H_2O, reflux. [m] $BrCH_2COOMe$, Zn (powder), I_2 (trace), Et_2O–C_6H_6, reflux, 2 h. [n] Ac_2O, pyr, room temp. [o] TsOH (trace), PhMe. [p] Pt. H_2, HOAc, room temp. [q] NaOH, MeOH, room temp. [r] TsOH (trace), C_6H_6, reflux.