Work is currently in progress in our laboratories to further investigate the role of the polymeric structure and conformation of DNA on the chemical reactions of the guanine radical cation, one of the two main intermediates of the direct effects of ionizing radiation.[23]

Acknowledgment. This work was supported in part by grants from the Ministry of Education, Science and Culture of Japan and from the "Commissariat à l'Energie Atomique". H.K. thanks the latter agency for providing financial support for his visit to Grenoble. We extend thanks to Drs. R. Bensasson and P. Heelis for stimulating discussions on triplet excited riboflavin and Dr. J.-C. Marchon for his review of the manuscript.

Supplementary Material Available: Experimental details of the photosensitization experiments and characterization of 7,8-dihydro-8-oxo-2'-deoxyguanosine (2 pages). Ordering information is given on any current masthead page.

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A Short Synthesis of (+)-Lycoricidine

Tomas Hudlicky* and Horacio F. Olivo

Department of Chemistry
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061-0212
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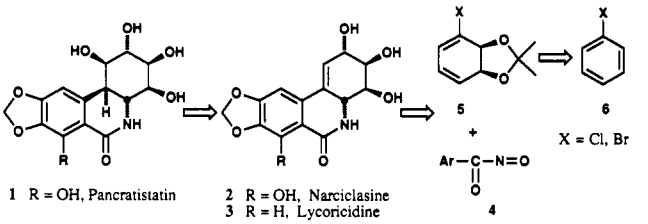
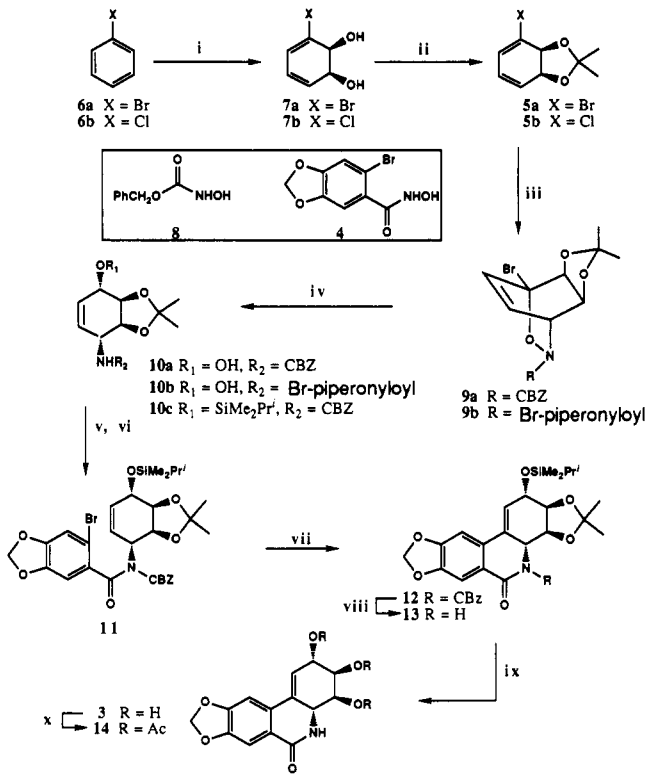
The narcissus alkaloids pancratistatin (**1**), narciclasine (**2**), and lycoricidine (**3**) are members of the Amaryllidaceae family and possess considerable medicinal potential because of their wide range of biological activities. Since their isolation in the late 1960s[1] and subsequent determination of their diverse cytotoxic properties,[2] there has been a focused effort to provide the most promising of these alkaloids, pancratistatin (**1**), to the medical community.[3] Extremely low natural abundance as well as practical complications in separation of the desired compound from other plant constituents diminishes the probability of reasonable supply of this and related compounds by means of isolation.[4] Clearly there is justification for synthetic effort in this area if the following criteria can be met: (a) cost-effective preparation, (b) environmentally benign synthetic protocol that would make the synthesis amenable to a large-scale production, and (c) stereorational and general design for all of the members of this class, especially the compounds named above.

Despite the many valiant synthetic approaches to these alkaloids[5] and several total syntheses,[6] no preparation of fewer than

Scheme I. A General Approach to Narcissus Alkaloids



Scheme II[a]



[a] Reagents: (i) *Pseudomonas putida*; (ii) DMP, acetone, *p*-TsOH; (iii) **4** or **8**, Bu_4NIO_4, CH_2Cl_2; (iv) Al(Hg), THF; (v) $ClSiMe_2Pr^i$, Im, CH_2Cl_2; (vi) BuLi, THF, -78 °C; then Br-piperonyloyl chloride; (vii) $Pd(OAc)_2$, Tl(OAc), DIPHOS, anisole; (viii) Pd(C), cyclohexene, EtOH; (ix) CF_3CO_2H, 0 °C, (x) Ac_2O, py.

* To whom correspondence should be addressed. Recipient of the American Cyanamid Faculty Research Award, 1992.

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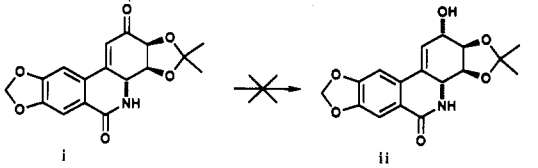

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15 synthetic operations has materialized to date.[7] Scheme I describes a general synthetic strategy for the preparation of these alkaloids; the strategy is characterized by the union of enantiomerically pure oxygenated diene **5**, derived biocatalytically from halobenzene **6**, with an appropriate acyl nitroso unit. In this paper we report the synthesis of lycoricidine (**3**) as the pivotal model system for the preparation of narcissus alkaloids.

Bromo- and chlorobenzenes **6** have been successfully oxidized[8] to cyclohexadiene *cis*-diols **7** (whose preparation in crystalline form is now an industrial process)[9] by means of the bacterial dioxygenase of *Psuedomonas putida*, Scheme II. The unique disposition of functionality in such cyclohexadienediols as **7** has been exploited by this research group in a general synthetic design of carbohydrates[10] and cyclitols,[11] including aminocyclitols.[12] Several other research groups have realized the synthetic potential of cyclohexadiene *cis*-diols in enantiocontrolled synthesis as evidenced by the increasing number of publications in this area.[13]

The polarization of the 1-halo 1,3-diene in **7** allows for regio- as well as stereospecific cycloadditions to various dienophiles,[14] including the acyl nitroso compounds generated in situ from hydroxamic acids. In addition, a remarkably stereospecific dimerization can take place with the C4–C5 double bond assuming the role of dienophile.[15] The use of acyl nitroso compounds as dienophiles in [4 + 2] cycloadditions is well documented[16] and is utilized in total synthesis.[17] On the other hand, the use of the 1-halocyclohexadiene unit in the Diels–Alder reaction has not been reported prior to our synthesis of conduramine-A1.[12a] An extensive study of the cycloadditions of several dienophiles with all four halo dienediols **5** (X = F, Cl, Br, I) was undertaken, and the regio- and stereochemical results were compared to theoretical predictions obtained from AM1 calculations.[18]

The synthesis of lycoricidine was carried out as follows. Acetonide **5a** was reacted with either **8** or **4** to produce oxazines **9a**[12a] and **9b** in 74% and 80% yields, respectively. Reduction of the bromine and the subsequent cleavage of the N–O bond were accomplished with aluminum amalgam at 0 °C[12b] (91%) with the preservation of the syn relationship of the C1 hydroxyl and the C4 nitrogen functionalities of aminoconduritols **10a** and **10b**.[12a] The reduction of **9b** to **10b** led, in several instances, to over-reduction and the loss of the aryl bromine atom. For this reason the CBZ-protected alcohol **10a**[12a] was alkylated with dimethylisopropylchlorosilane in 98% yield and converted to amide **11** (77%) by acylation of the lithium amide with 2-bromopiperonyloyl chloride,[19] in addition to attaining amide **11** directly by silylation and CBZ-protection of **10b**. Closure of **11** was attempted by several methods including atom-transfer conditions of the radical cyclization,[20] trans metalation and intramolecular opening of its epoxide,[21] and the Pd-catalyzed Heck reaction.[22] While this work was in progress, a diastereomer of this compound was reported by Chida and Ogawa to undergo a Heck-type closure.[6d] Despite the availability of full experimental details for this transformation, kindly furnished to us by Professor Chida,[23] we were not able to reproduce the conditions of this transformation. The closure of **11** to **12a** was finally accomplished in 27% yield by means of a modified Heck cyclization with $Pd(OAc)_2$, Tl(OAc), and 1,2-bis(diphenylphosphino)ethane in anisole.[23,6d] The major byproducts of the reaction included desilylated and trans-acetylated derivatives of **12**, all of which can be transformed to lycoricidine, making the overall yield of the cyclization 70–80%. The cyclized amide **12** was easily deprotected by means of palladium on carbon in a mixture of cyclohexene and ethanol to yield amide **13** (99%). Treatment of this material with trifluoroacetic acid at 0 °C afforded, in 85% yield, lycoricidine (**3**), whose physical, optical, and spectral properties matched those reported in the literature.[6a,c,d] Its structure was further confirmed by conversion of **3** to its acetate **14** (whose structure proof rests on X-ray crystallography)[6a,c] and comparison of its spectra to those kindly furnished to us by Chida.

In summary, the synthesis of lycoricidine in nine steps demonstrates the potential viability of this approach to narcissus alkaloids. Further research will address the chemical oxidative conversion of lycoricidine to deoxypancratistatin and either a direct

(7) The total syntheses of **3** published to date, while academically elegant, are not suited for a realistic provision of **3** on a large scale. The starting material, the number of steps and the overall yield, as reported, are tabulated below:

Starting Material	Number of Steps	Overall Yield (%)	Reference
Piperonal	19	1.5	6a
Piperonal	17	7.2	6b
Glucose	13	3.9	6c
Glucose	24	0.042	6d

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enzymatic hydroxylation of the aromatic ring or incorporation of the phenolic hydroxyl to the aryl precursor **4** as suitable modifications for the synthesis of pancratistatin (**1**). We will report on the progress toward this goal in due course.

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Supplementary Material Available: Experimental procedures and spectral data (^{1}H-NMR and ^{13}C-NMR) for compounds **9b**, **10b,c**, **11-13**, and **3** (4 pages). Ordering information is given on any current masthead page.

Jahn-Teller Distortion Predicted for Metallocarbohedrenes: An ab Initio SCF Geometry Optimization of the Lowest Singlet and Triplet States of Ti_8C_{12} in the T_h and D_{2h} Point Groups

Marie-Madeleine Rohmer, Pieter de Vaal,† and Marc Bénard*

Laboratoire de Chimie Quantique, UPR 139 du CNRS Institut Le Bel, F-67000 Strasbourg, France

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The existence of a new class of stable clusters has just been postulated from the exceptional abundance of the ionic species $M_8C_{12}^+$ (M = Ti, V) in the distribution of metal-carbon clusters obtained from reactions of the metal with hydrocarbons.[1-3] It has been proposed that the prominence of the M_8C_{12} cluster arises due to its presence as a neutral species. The unusual stability of M_8C_{12} is taken as a strong argument in favor of the cagelike structure of the pentagonal dodecahedron with T_h symmetry proposed by Guo et al.,[1-3] which is reminiscent of another cage structure with exceptional stability, the famous buckminsterfullerene, C_{60}.

We report the first quantum chemical calculations on Ti_8C_{12}. Those calculations have been carried out at the ab initio SCF level[4] using the ASTERIX program system.[7] Since no experimental structure is available yet, the geometry of the lowest closed-shell singlet state has been optimized using an analytical gradient technique.[8] In a first series of calculations, the constraints of the T_h symmetry point group have been imposed along the complete process of geometry optimization. Accounting for the 80 valence electrons, the lowest singlet state in the T_h symmetry can be labeled as

$$^1A_g \qquad (4a_g)^2(1a_u)^2(3e_g)^4(1e_u)^4(3t_g)^6(6t_u)^6 \qquad (1)$$

Only three geometrical parameters are independent under the constraints of the T_h group and require optimization, namely, the radius of the "metal sphere" containing all Ti atoms, the radius of the carbon sphere, and the C-C distance. The optimal values for those parameters and for the corresponding Ti-Ti and Ti-C distances are reported in Table I. The HOMO, $4a_g$, corresponds to a poorly stabilized, in-phase combination of the metal 4s orbitals, with negligible contribution (4%) from the carbons. The low-lying LUMO, $4t_g$, results from a stabilizing interaction between the carbon π^* orbitals and appropriate combinations of the d_{x^2,y^2,z^2} metal orbitals. It immediately appears from the weak HOMO-LUMO gap (0.063 hartree or 1.7 eV; Table I) that the promotion of an electron pair from $4a_g$ to the triply degenerate orbital $4t_g$ will lead to a stabilized triplet state. As a matter of fact, two low-lying triplet states have been characterized at the open-shell SCF level of calculation by populating $4t_g$ with either two or four electrons. The corresponding states are labeled as

$$^3T_g \qquad (3a_g)^2(1a_u)^2(3e_g)^4(1e_u)^4(4t_g)^2(6t_u)^6 \qquad (2)$$

and

$$^3T_g \qquad (3a_g)^2(3e_g)^4(1e_u)^4(4t_g)^4(6t_u)^6 \qquad (3)$$

and the total energies respectively associated with states 2 and 3 at their optimal geometries are lower by 0.171 and 0.233 hartree than that of state 1 (Table I).

In state 3, the energy gaps separating the HOMO from the partly occupied molecular orbitals (POMO), on the one hand, and the POMO from the LUMO, on the other hand, are large enough to suggest that the considered state is the lowest state of the Ti_8C_{12} cage *as far as the symmetry constraints of the T_h point group are applied to the wave function.*

As shown by Jahn and Teller,[9] degenerate electronic states such as states 2 and 3 cannot exist, except for linear molecules, since they cause structural instability. In order to explore the effect of this first-order Jahn-Teller (FOJT) distortion, the degenerate character of the wave function was removed by allowing the four electrons equally distributed in the triply degenerate POMO to be accommodated in two orbitals only, thus giving rise to a closed-shell singlet configuration with D_{2h} symmetry:[10]

$$^1A_g \qquad (9a_g)^2(4b_{1g})^2(4b_{2g})^2(3b_{3g})^2(2a_u)^2(6b_{1u})^2(6b_{2u})^2(6b_{3u})^2 \qquad (4)$$

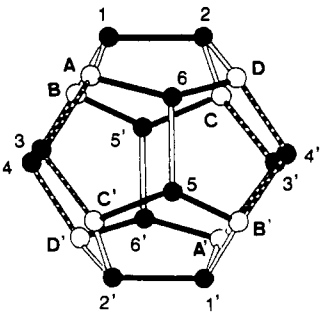

Figure 1. Computed structure of the Ti_8C_{12} cage molecule along the D_{2h} distortion path. White circles, labeled A-D, correspond to titanium atoms; black circles, labeled 1-6, to carbon atoms. Bold lines represent short bonds (carbon-carbon, 1-2 = 1.299 Å; titanium-carbon, A6 = D6 = B5′ = C5′ = 1.952 Å); thin lines represent long bonds (C-C, 5-6 = 1.478 Å; Ti-C: A1 = B1 = C2 = D2 = 2.145 Å); broken lines represent intermediate bonds: (C-C: 3-4 = 1.392 Å; Ti-C: A3 = B4 = C3′ = D4′ = 2.067 Å). The Ti-Ti distances are as follows: BC = AD = 3.033 Å; AC′ = BD′ = 3.198 Å; AB = CD = 3.275 Å (see Table I). When a T_h symmetry is assumed for the cage, all C-C bonds, all Ti-C bonds, and all Ti-Ti distances become equivalent.

† Permanent address: Gerbrandylaan 45, 2253 LA Voorschoten, The Netherlands.

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