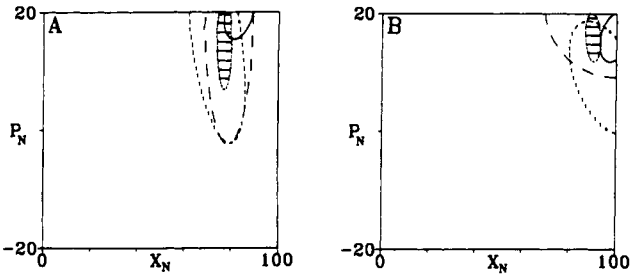

Figure 2. The 90% confidence limits, based on the formal covariance matrices on the assumption of normally distributed errors,[13] of (X_N, P_N) after minimization (see text) for H1′ TOCSY ladder intensities obtained at 35 ms (···), 95 ms (– – –), and seven different mixing times between 20 and 110 ms (—); shaded areas are for sets of experimental J-couplings, given in the caption below Figure 1, for (A) the cytidine and (B) the guanosine sugar ring spin system in cd(CpGp).

respectively, and the pucker amplitudes in the range $30° < \Phi_N, \Phi_S < 40°$.[1,10,11] The average sugar ring conformation can thus be described in terms of P_N, P_S, Φ_N, Φ_S, and X_N, the fraction N conformer. The J-couplings for the pure N and S conformations can be derived by means of the EOS Karplus equations, while the set of effective J-couplings of the average sugar conformation is the weighted average of the J-couplings of the pure N and S conformers.[1,10-12] Thus, instead of describing the TOCSY coherence transfer in terms of the effective J-couplings, we may describe it directly in terms of the sugar ring conformational parameters, which has the advantage of introducing independent and physically interpretable parameters. To determine these parameters from the experimental TOCSY data, the nonlinear least-squares algorithm of Marquardt[13] was used. To avoid excessive use of the time-consuming TOCSY simulation in the iterative fitting process, we constructed, in advance, a database of simulated TOCSY data, which was subsequently used as a model data grid in the Marquardt algorithm. We demonstrate the approach using only H1′ TOCSY connectivities, to give an indication of the results obtained with a limited number of experimental intensities, and because the H1′ resonances are generally less likely to overlap. Even if the direct H1′H2′ cross peak overlaps, preventing COSY cross peak simulation, the approach proposed here still works, as it is unlikely that all of the relay peaks will do so as well. In the fitting procedure we kept $\Phi_{S,N}$ and P_S fixed at 35° and 162°, respectively, leaving P_N and X_N as adjustable parameters. In Figure 2 the results of these minimizations are given and compared with those obtained with the usually applied procedure,[1,3,11,12,14] which is to establish P_N and X_N from J-couplings determined from COSY cross peak fine structure or, herer, 1D spectra. To aid in the comparison for the latter, an (analogous) Marquardt fitting procedure was used. Examination of Figure 2 shows that the accuracy of the values derived for P_N is about the same for the values obtained from the J-coupling and TOCSY data, in the latter case depending somewhat on the mixing times involved. A similar remark can be made with respect to the value of the fraction N conformer, X_N.

The present result shows that it is possible to obtain accurate structure parameters from TOCSY data. This is of particular interest for future quantitative evaluation of structural features in (bio)macromolecular systems for which accurate J-coupling data cannot be obtained directly but where TOCSY still yields good quality spectra.

Acknowledgment. The computer processing was carried out at computer facilities of the SON/NWO National HF-NMR Facility at Nijmegen. This work was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Advanced Research (NWO).

Total Synthesis of (+)-Duocarmycin SA

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(+)-Duocarmycin SA (**1**),[2] a naturally occurring and exceptionally potent antitumor antibiotic, represents the newest and most potent member of a growing class of agents[3,4] that derive their biological properties through a sequence-selective minor groove alkylation of duplex DNA.[5] Because of its enhanced solvolytic stability[2] relative to (+)-duocarmycin A[3] and (+)-CC-1065,[6] the examination of (+)-duocarmycin SA[7] promises to be especially interesting. Herein, we report the first total synthesis of (+)-duocarmycin SA based on sequential regioselective nucleophilic substitution reactions[8] of the unsymmetrical *p*-quinone diimide **3** in the preparation of a functionalized dihydropyrroloindole precursor to its alkylation subunit. In addition to constituting a new synthetic strategy for the preparation of natural or synthetic members of this growing class of agents,[9-14] both

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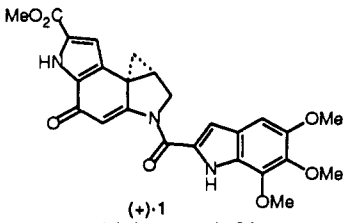
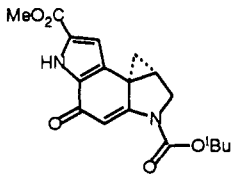
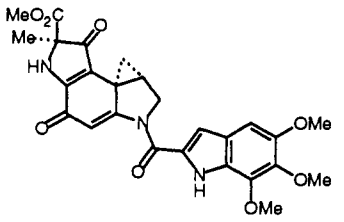
enantiomers of **2** (*N*-BOC-DSA) and its immediate precursors may be made available through the approach which provides access to analogs incorporating either enantiomer of the exceptionally stable alkylation subunit.



(+)-1
(+)-duocarmycin SA



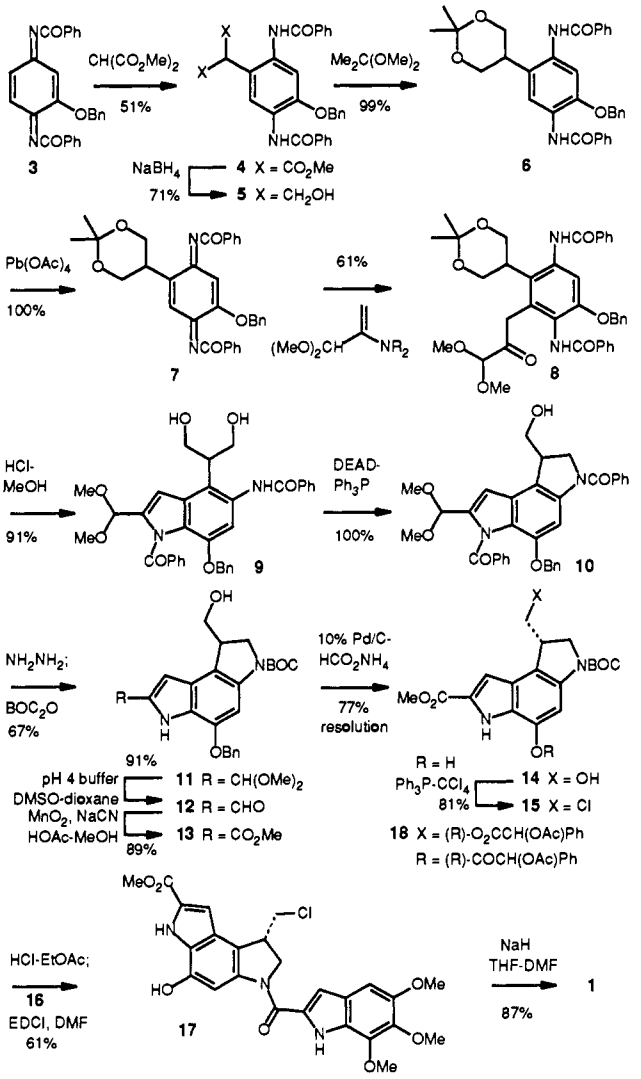
(+)-2
(+)-N-BOC DSA



(+)-duocarmycin A

Treatment of **3**[8] with dimethyl malonate (1.1 equiv, 0.3 equiv of $NaOCH_3$, THF, −30 °C, 2 h, 51–64%) provided **4**[8] derived from regioselective C5 nucleophilic addition attributable to steric and electronic deactivation of addition at C3 or C6 by the C2 benzyloxy substituent (Scheme I). Methyl ester reduction (5 equiv of $NaBH_4$, EtOH, 0–25 °C, 3 h, 71%), protection of diol **5** as the acetonide **6** (2 equiv of $Me_2C(OMe)_2$, catalytic TsOH, DMF, 25 °C, 24 h, 99%), and oxidation (1 equiv of $Pb(OAc)_4$, $CHCl_3$, 0–25 °C, 2.5 h, 100%) provided **7** and a suitable acceptor substrate for a second nucleophilic substitution reaction. Clean regioselective C6 nucleophilic addition of the pyrrolidine enamine of pyruvaldehyde dimethyl acetal[15] was achieved (2 equiv, THF, 25 °C, 10–15 min) if followed immediately by mild acid treatment under defined reaction conditions (40 mL of THF–10 mL of pH 4 phosphate buffer/mmol, 25 °C, 4–24 h) to provide **8** cleanly (61%). Competitive or predominant C1 or C4 nucleophilic addition or *p*-quinone diimide reduction was observed with a number of examined nucleophiles, and alternative hydrolysis conditions generally provided a mixture of products derived from **8** including **9**. Treatment of **8** with HCl (2 equiv, CH_3OH, 25 °C, 2 h, 91%) provided **9** resulting from acid-catalyzed indole formation and concurrent acetonide hydrolysis without competitive indole *N*-benzoyl deprotection or acetal hydrolysis. Completion of the

Scheme I



preparation of the functionalized dihydropyrroloindole skeleton was accomplished by cyclization of diol **9** under Mitsunobu[16] alkylation conditions (1.5 equiv of DEAD–Ph_3P, THF, 25 °C, 2 h, 100%) to provide **10**.

Deprotection of the benzamides (67% NH_2NH_2–EtOH, reflux, 18–24 h) followed by reprotection of the indoline C3 amine (3 equiv of BOC_2O, THF, 25 °C, 30 min) provided **11** (67% overall). Mild acid-catalyzed hydrolysis of the dimethyl acetal under carefully prescribed reaction conditions (DMSO–pH 4 phosphate buffer–dioxane 1:2:12, reflux, 15 h, 91%) provided **12** in excellent yield *without* competitive BOC deprotection, and subsequent oxidation[17] (5 equiv of MnO_2, 5 equiv of NaCN, 0.2 equiv of HOAc, CH_3OH, 25 °C, 89%) provided the methyl ester **13**. Two-phase, transfer catalytic hydrogenolysis[18] (0.45 wt equiv of 10% Pd–C, 25% aqueous HCO_2NH_4–THF 1:30, 25 °C, 2 h, 77%) served to remove the benzyl ether and provided **14**. Conversion[19] of **14** to the chloride **15** (3 equiv of PPh_3, 9 equiv of CCl_4, CH_2Cl_2, 25 °C, 3 h, 81%) followed by treatment with NaH (3 equiv, THF–DMF 1:2, 0 °C, 30 min, 85%) provided *N*-BOC-DSA (**2**). Acid-catalyzed deprotection of **15** (3 N HCl–EtOAc, 25 °C, 20 min) followed by coupling of the indoline hydrochloride salt with 5,6,7-trimethoxyindole-2-carboxylic acid[5] (**16**, 3 equiv of EDCI, 4 equiv of $NaHCO_3$, DMF, 25 °C, 15 h, 61%) provided **17**. Final

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intramolecular Ar-3′ alkylation of **17** with closure of the cyclopropane ring provided duocarmycin SA in excellent yield (3 equiv of NaH, THF–DMF 1:2, 0 °C, 30 min, 87%), and the properties of synthetic **1** proved identical (^{1}H NMR, ^{13}C NMR, IR, UV, MS/HRMS) or comparable ($[\alpha]_D$) with those reported for the natural material.

Resolution of **14** was accomplished by conversion to the bis-(*R*)-*O*-acetylmandelate ester **18** following past protocols[8,12,13] (2.5 equiv of (*R*)-PhCH(OAc)CO_2H, 3.0 equiv of EDCI, 0.1 equiv of DMAP, CH_2Cl_2, 25 °C, 2.5 h, 85%) and chromatographic separation of the resulting diastereomers (preparative HPLC, α = 1.31, 5:95 EtOAc–CH_2Cl_2, 250 × 22.5 mm Alltech 10 μm SiO_2) to provide 1(*S*),2′(*R*),2″(*R*)-**18** and 1(*R*),2′(*R*),2″(*R*)-**18**. Independent hydrolysis of the separated diastereomers (2.5 equiv of NaOMe, MeOH, 0 °C, 1 h, 93%) provided (−)-1(*S*)-**14** possessing the natural configuration of (+)-duocarmycin SA and (+)-1(*R*)-**14**. The conversion of (−)-1(*S*)-**14** to (−)-1(*S*)-**15** and (+)-*N*-BOC-DSA (**2**, $[\alpha]^{22}_D$ +144° (*c* 0.06, CH_3OH)) and incorporation into natural (+)-duocarmycin SA ($[\alpha]^{22}_D$ +197° (*c* 0.035, CH_3OH), lit[2] $[\alpha]^{24}_D$ +180° (*c* 0.1,[20] CH_3OH)) followed the sequence detailed in Scheme I.

The examination of the properties of (+)- and (−)-**1** and the preparation of analogs incorporating the DSA alkylation subunit are in progress and will be reported in due course.

Acknowledgment. We gratefully acknowledge the financial support of the National Institutes of Health (CA 55276) and Dr. I. Takahashi, Kyowa Hakko Kogyo Co., Ltd., for copies of the ^{1}H NMR spectrum of natural duocarmycin SA and a summary of its physical and spectroscopic properties.

Supplementary Material Available: Listings of the full characterization of **1–2**, **4–15**, and **17–18** (10 pages). Ordering information is given on any current masthead page.

(20) Synthetic (+)-duocarmycin SA was not completely soluble at this concentration, and this may account for the slightly lower rotation reported for the natural material.

A High-Nuclearity Polyoxoalkoxomolybdate Cluster Encapsulating a $[Na(H_2O)_3]^+$ Moiety. Hydrothermal Synthesis and Structure of $[Na(H_2O)_3H_{15}Mo_{42}O_{109}\{(OCH_2)_3CCH_2OH\}_7]^{7-}$

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While the chemistries of both the polyoxometalate anions[1] and the polynuclear metal alkoxides[2] have received considerable contemporary attention, the related polyoxoalkoxometalate clusters remain largely unexplored. Despite the emergent nature of this chemistry, a variety of "oxidized" clusters, of which $[Ti_7O_4(OEt)_{20}]$[3] and $[Nb_8O_{10}(OEt)_{20}]$[4] are prototypical, and of reduced

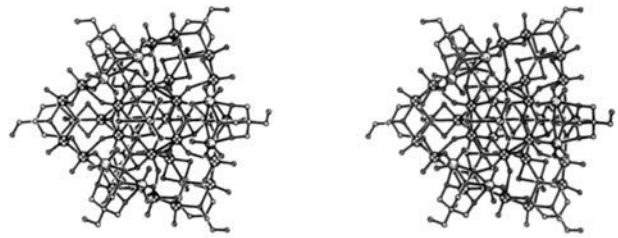

Figure 1. A stereoview of the molecular anion **1a** approximately along the normal to the central $\{Mo_6O_{24}\}$ moiety, showing the idealized C_3 symmetry of the structure. Open bonds are used to illustrate the 18 Mo(V)–Mo(V) interactions. Mo(V) centers are shown as crosshatched spheres, while the six Mo(VI) sites are shown as stippled spheres. The central Na^+ cation is shown as a sphere with parallel diagonal lines.

and mixed-valence polynuclear cores, such as $[Mo_4O_8(OR)_4(pyridine)_4]$[5] and $[Mo_6O_{10}(OR)_{12}]$,[6] have been reported, suggesting that polyoxoalkoxometalates may provide a novel class of clusters with unusual structural and electronic variety. Furthermore, it has been noted that the high-nuclearity polyoxoalkoxomolybdate $[Mg_2Mo_8O_{22}(OR)_6(HOR)_4]^{2-}$[7] possesses cavities for the incorporation of electropositive cation groups, in a manner reminiscent of the encapsulation of a variety of small guest molecules by polyoxovanadate clusters.[8] As part of our studies of the coordination chemistry of polyoxometalates with alkoxide ligands,[9] we have noted that tris(alkoxy) ligands of the general class $(HOCH_2)_3CR$ are effective in stabilizing triangular units $\{M_3O_n[(OCH_2)_3CR]\}$, which may in turn aggregate to form high-nuclearity clusters. By combining this feature with the solubility and crystallization advantages afforded by hydrothermal synthesis, we have isolated and structurally characterized a novel mixed-valance cluster, $[Na(H_2O)_3H_{15}Mo^V_{36}Mo^{VI}_6O_{109}\{(OCH_2)_3CCH_2OH\}_7]^{7-}$, a basket type structure encapsulating a $\{Na(H_2O)_3\}^+$ moiety.

The reaction of MoO_3, $Na_2MoO_4{\cdot}2H_2O$, $C(CH_2OH)_4$ (pentaerythritol, H_4L), $(Et_4N)Cl$, Me_3NHCl, and water in the molar ratio 6:6:10:10:10:300 at 160 °C for 3 days gave diamagnetic red-brown crystals of $(Me_3NH)_2(Et_4N)Na_4[Na(H_2O)_3H_{15}Mo_{42}O_{109}\{(OCH_2)_3CCH_2OH\}_7]{\cdot}15H_2O$ (**1**·15H_2O) in 30% yield.[10] The X-ray structure of **1** revealed the presence of the discrete molecular anion $[Na(H_2O)_3H_{15}Mo_{42}O_{109}\{(OCH_2)_3CH_2OH\}_7]^{7-}$ (**1a**), shown in Figure 1.[11] The structure consists of a framework of edge- and corner-sharing $\{MoO_6\}$ octahedra with the organic residues projecting outward from the central core. The anion may be most conveniently described in terms of the three structural motifs shown in Figure 2. Four of the pentaerythritol ligands, HL^{3-}, coordinate in the usual tridentate bridging mode to a triangular arrangement of three Mo(V) centers, which in turn are each associated through edge-sharing of oxo groups to an adjacent Mo(V) site (**1b**); the Mo–Mo distances within these binuclear units are in the 2.55–2.65-Å range, corresponding to metal–metal single bonds for Mo. The second

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(10) Anal. Calcd for $C_{49}H_{154}Mo_{42}N_3Na_5O_{155}$: C, 7.93; H, 2.08; N, 0.57; Mo, 54.4. Found: C, 7.30; H, 1.95; N, 0.33; Mo, 54.2. IR (KBr pellet, cm^{-1}): 1112 (vs), 1061 (m), 1021 (vs), 986 (vs), 911 (m), 886 (m), 810 (sh).

(11) Crystal data for $C_{49}H_{154}Mo_{42}N_3Na_5O_{155}$ (**1**): triclinic space group $P\bar{1}$, a = 22.159 (4) Å, b = 27.049 (5) Å, c = 17.726 (3) Å, α = 98.34 (1)°, β = 112.56 (2)°, γ = 82.81 (1)°, V = 9680 (3) $Å^{-3}$, Z = 2, D_{calcd} = 2.542 g cm^{-3}, D_{obsd} = 2.51 (2) g cm^{-3}. Structure solution and refinement based on 20028 reflections converged at R = 0.066. The solvent system is disordered, and some water molecules are highly smeared. The formula is, therefore, approximately **1**·15H_2O.

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