dipolarophile, some diastereoselection was observed (6β, 2:1), using 2β as the nitrile oxide precursor. The nitrile oxide from 2α gave, on the other hand, a 1:1 mixture of separable diastereomers 6α.

In conclusion, when one considers all of the other known ways to manipulate isoxazoles, such as ring metalation, as well as the variety of ring-opening processes known for the isoxazolium salts (especially the 5-unsubstituted derivatives),[13] then numerous possibilities can be envisioned for the use of such nitrile oxides in the design of new *C*-nucleoside analogues. We further suggest that this general concept of constructing nitrile oxides containing sugars and sugar fragments should find broader applications in synthesis, for it is possible to effect carbon–carbon bond formation with creation of a masked β-hydroxy ketone from a chiral fragment containing an α-oxygen substituent.[14] This would, of course, be difficult to achieve through conventional carbanion chemistry because of competing β-elimination processes. Other reports concerning this situation will be forthcoming.

Acknowledgment. We are indebted to the National Institutes of Health (Grant No. HL-20579) for support of these investigations.

Registry No. 1α, 79698-06-9; 1β, 79733-40-7; 2α, 84987-81-5; 2β, 85027-42-5; 3α, 84987-82-6; 3β, 84987-83-7; 4α, 84987-84-8; 4β, 84987-85-9; 5, 84987-86-0; 6α, 84987-87-1; 6β, 84987-88-2; ethoxyethyne, 927-80-0; phenylethene, 100-42-5; hydrazine, 302-01-2.

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(14) For a leading reference on the use of monosaccharide nitrones in synthesis, chemistry related in a sense to that described herein, see: Vasella, A.; Voeffray, R. *Helv. Chim. Acta* **1982**, *65*, 1134.

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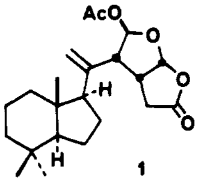
Norrisolide, a Novel Diterpene from the Dorid Nudibranch *Chromodoris norrisi*[1]

Summary: The dorid nudibranch *Chromodoris norrisi* contains an unusual rearranged diterpene, norrisolide (1). The structure of norrisolide was determined by X-ray diffraction analysis.

Sir: As part of a study of the chemical defense mechanism of nudibranch molluscs,[2] we have examined the chemical constituents of the common dorid nudibranchs from the Gulf of California. Most dorid nudibranchs contained metabolites either identical with or closely related to known sponge metabolites.[3] A notable exception to this observation was the discovery of the unusual diterpene norrisolide (1) from the brightly colored dorid nudibranch *Chromodoris norrisi* Farmer 1963.[4] In this paper we report the structural elucidation of norrisolide (1) by a single-crystal X-ray diffraction experiment.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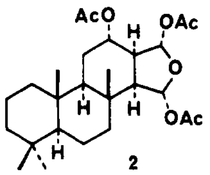
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Ten specimens of *Chromodoris norrisi* (average weight 0.2 g) were collected near San Carlos Bay, Sonora, Mexico, and were stored in acetone for 2 weeks. The dichloromethane-soluble material from the decanted acetone was twice chromatographed by LC on Partisil first with ether and then with 2:1 ether/hexane as eluants to yield norrisolide (1, 0.2 mg/animal) as small colorless crystals, mp 138–140 °C.

Norrisolide (1) had the molecular formula $C_{22}H_{32}O_5$. The mass spectrum showed a very weak molecular ion peak at *m/z* 376 with strong peaks at *m/z* 316 and 317, indicating facile loss of an acetate group. The infrared spectrum contained bands at 1800 (γ-lactone) and 1760 cm^{-1} (acetate). The ^{13}C NMR spectrum[5] contained two carbonyl signals at δ 173.6 (s) and 168.6 (s), two acetal carbon signals at δ 107.1 (d) and 101.8 (d), and signals for an α,α′-disubstituted olefin at δ 143.5 (s) and 116.8 (t). A series of ^1H NMR decoupling experiments defined the oxygen-containing portion of the molecule: a two-proton signal at δ 2.55 (d, 2 H, *J* = 7 Hz, C-13) was coupled to a signal at δ 3.36 (m, 1 H, *J* = 9.5, 7, 7, 6 Hz, C-12) that was in turn coupled to an acetal proton signal at δ 6.14 (1 H, d, *J* = 6 Hz, C-20) and a methine proton signal at δ 3.07 (dd, 1 H, *J* = 9.5, 3.5 Hz, C-11) that was further coupled to the second acetal proton signal at δ 6.44 (d, 1 H, *J* = 3.5 Hz, C-19). The chemical shift of the δ 3.07 signal and the absence of further coupling suggested that the α,α′-disubstituted olefin was located at C-10. Since the ^1H NMR spectrum[5] contained three methyl signals at δ 0.66 (s, 3 H), 0.84 (s, 3 H), and 0.86 (s, 3 H) and the molecular formula required an additional two carbocyclic rings from the nine remaining carbon atoms, these data indicated that norrisolide contained a novel diterpene ring system.

The structure of norrisolide (1) was determined by a single-crystal X-ray diffraction experiment.[6] A comput-

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(4) Farmer, W. M. *Trans. San Diego Soc. Nat. Hist.* **1963**, *13*, 31.

(5) IR (CCl_4) 1800, 1760, 1370, 1215 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.66 (s, 3 H), 0.84 (s, 3 H), 0.86 (s, 3 H), 2.07 (s, 3 H), 2.55 (2 H, d, *J* = 7 Hz), 3.07 (dd, 1 H, *J* = 9.5, 3.5 Hz), 3.36 (m, 1 H, *J* = 9.5, 7, 7, 6 Hz), 5.09 (br s, 1 H), 5.15 (br s, 1 H), 6.14 (d, 1 H, *J* = 6 Hz), 6.44 (d, 1 H, *J* = 3.5 Hz); ^{13}C NMR (C_6D_6) δ 173.6 (s), 168.6 (s), 143.5 (s), 116.8 (t), 107.1 (d), 101.8 (d), 58.8 (d), 57.8 (d), 50.1 (d), 45.1 (s), 41.8 (t), 40.6 (d), 38.7 (t), 33.5 (q), 33.3 (s), 30.5 (t), 24.3 (t), 21.2 (t), 20.7 (q), 20.5 (t), 19.9 (q), 14.2 (q); HRMS, obsd *m/e* 316.2047, $C_{20}H_{28}O_3$ (M − AcOH) required *m/e* 316.2038.

(6) Preliminary X-ray diffraction patterns showed monoclinic symmetry and accurate lattice constants of $a = 12.691$ (2) Å, $b = 7.517$ (2) Å, $c = 22.531$ (3) Å and $\beta = 108.24$ (7)°. Systematic extinctions and density were most plausibly accommodated by space group *C*2 with one molecule of $C_{22}H_{32}O_5$ in the asymmetric unit. All unique diffraction maxima with $2\theta \leq 114°$ were collected on a four-circle diffractometer by using graphite monochromated Cu Kα radiation (1.541 78 Å) and 1° ω scans. A total of 1578 reflections was collected in this fashion, and after correction for Lorentz, polarization, and background effects 1447 (92%) were judged observed ($|F_o| \geq 3\sigma(R_o)$). A phasing model was deduced by standard multisolution direct methods and extended by tangent formula recycling.[7] This revealed the entire nonhydrogen structure, and 29 of the hydrogens were located by a difference synthesis after partial refinement. The remaining hydrogens were included at calculated positions, and block-diagonal least-squares refinement with anisotropic nonhydrogen atoms and isotropic hydrogens has converged to a standard residual of 0.058 for the observed reflections. Additional crystallographic details can be found in the supplementary material.

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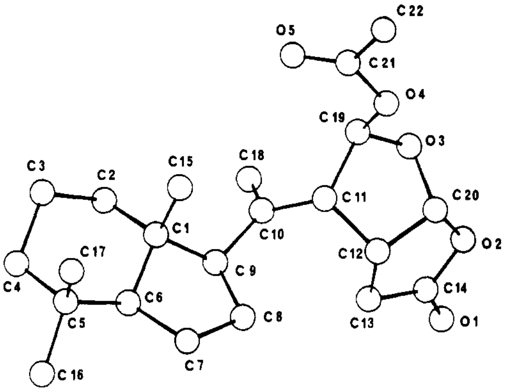

Figure 1. Computer-generated perspective drawing of norrisolide (1). Hydrogens are omitted for clarity, and the enantiomer shown is arbitrary.

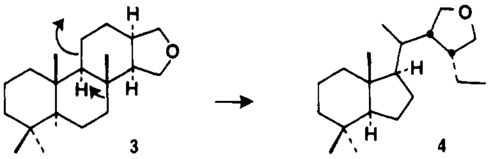

Figure 2. Proposed biosynthesis of the norrisane skeleton.

er-generated perspective drawing less the hydrogens of the final X-ray model of norrisolide (1) is shown in Figure 1. The X-ray experiment did not define the absolute configuration, and the enantiomer shown is an arbitrary choice, the same as that determined for isoagatholactone, a diterpene of known absolute stereochemistry from *Spongia officinalis*.[8,9] There is a perhydroindane bicyclic system with an axial methyl and hydrogen at the bridgeheads. The cyclohexane ring is in the chair conformation, and the conformation of the cyclopentane ring is intermediate between the half-chair and envelope configurations.

After completing this study, we found norrisolide (1) as a very minor constituent of the sponge *Dendrilla* sp. collected at Palau, Western Caroline Islands, but we have been unable to find this or related sponges in the Gulf of California. *Dendrilla* sp. is closely related taxonomically to *Aplysilla rosea* from which Kazlauskas et al.[10] obtained aplysillin (2). We therefore propose that the norrisane skeleton (4) was derived from the spongian[11] skeleton (3) by opening of ring C with concomitant contraction of ring B, a process that results in the observed relative stereochemistry (Figure 2).[12]

Acknowledgment. Specimens were identified by James R. Lance and Janice E. Thompson. The research was supported by grants from the National Science Foundation (CHE-8121471), National Institutes of Health (CA-24487), and New York Sea Grant Program.

Registry No. 1, 85066-78-0.

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, bond distances, bond angles, and torsion angles (7 pages). Ordering information is given on any current masthead page.

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Synthesis of Optically Active β-Lactams from Serinylphenylserine. A Convenient Route to Nocardicins and Monobactams[1]

Summary: Chiral synthesis of 3-amido-2-azetidinones has been achieved in good yield by the reaction of L-serinylphenylserine with triphenylphosphine and diethyl azodicarboxylate. These β-lactams can be easily converted to N-unsubstituted β-lactams which are convenient intermediates for nocardicins and monobactams.

Sir: Monocyclic β-lactams[2] have become subjects of renewed attention from synthetic and medicinal chemists since the discovery in nature of nocardicins[3] and monobactams.[4,5]

The absolute configuration of at least one of the β-lactam carbons is of critical importance for antibacterial activity.[6] The value of a synthetic approach to a β-lactam is therefore enhanced if the synthesis leads to an optically active compound with control of the relative configuration of the various asymmetric centers in the molecule. We describe here a convenient synthesis of optically active 3-amino-2-azetidinones starting with readily available derivatives of serinylphenylalanine.

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[2] For reviews see: Manhas, M. S.; Bose, A. K. "Beta-Lactams—Natural and Synthetic"; Wiley-Interscience: New York, 1971. Christensen, B. G.; Ratcliffe, R. W. *Annu. Rep. Med. Chem.* **1976**, *11*, 271.

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