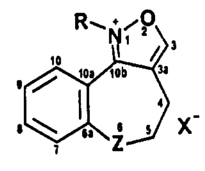
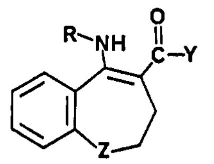
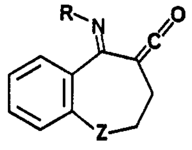


8a, Z = CH$_2$; R = Et; X = FSO$_3$
8b, Z = CH$_2$; R = t-Bu; X = ClO$_4$
8c, Z = CH$_2$; R = 1-Ad; X = ClO$_4$
8d, Z = CH$_2$; R = t-Bu; X = BF$_4$
8e, Z = CH$_2$; R = 1-Ad; X = BF$_4$
8f, Z = O; R = Me; X = CF$_3$SO$_3$



9a, Z = CH$_2$; R = Et; Y = NEt$_2$
9b, Z = CH$_2$; R = 1-Ad; Y = OMe
9c, Z = CH$_2$; R = 1-Ad; Y = NEt$_2$
9d, Z = O; R = Me; Y = OMe
9e, Z = O; R = Me; Y =)$_2$O

min). Similar results were obtained with the *tert*-butyl salt (**8b** → **11b**, lifetime ca. 10 min) and the adamantyl salt (**8c** → **11c**, lifetime ca. 20 min).



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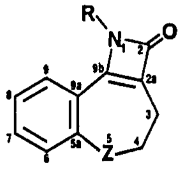

11

a, Z = CH$_2$; R = Et
b, Z = CH$_2$; R = t-Bu
c, Z = CH$_2$; R = 1-Ad
d, Z = O; R = Me

FT IR studies fixed the C=O position of **11c** at 5.56 μm (vs. 5.55 μm for **1** R = 1-adamantyl[1]). Quite stable solutions of **11c** could be obtained at the lower temperatures permitted in ^{13}C NMR analysis. i-Pr$_2$NEt (1 equiv) was added to a −78 °C solution of **8c** in anhydrous 1:1 CH$_2$Cl$_2$:CDCl$_3$ in an NMR tube then placed in a probe kept at −40 °C. After 2 h, the ^{13}C NMR spectrum contained only peaks of **11c** downfield from CDCl$_3$: C$_2$ 177.0, C$_{9b}$ 170.5, C$_{2a}$ 144.6, C$_{5a}$ and C$_{9a}$ 128.6 and 124.3, C$_{6-9}$ 130.8, 129.1, 127.9, and 125.1 ppm.[13] After another 2 h at −20 °C, the spectrum was unchanged. However, after a few min at 25 °C, **11c** had decomposed to a mixture of products. In similar experiments with **8a** and **8f**, the solutions of **11a** (C$_2$ 175.4, C$_{9b}$ 166.7, C$_{2a}$ 141.9) and **11d** (C$_2$ 173.3) were much less stable and contaminated from the start with decomposition products.

The solutions of **11a–c** all gave complex mixtures of products unless nucleophiles were quickly added to the reaction media (→ **9**). The relative lifetimes of **11a–c** reflect steric differences in the accessibility of **11** to :Nu and probably also variations in the peri interaction with C$_9$H helping to keep the ring closed. In accord with this rationalization, *N*-methylazetinone (**11d**) was too unstable to detect by IR.[14]

Since **2** does not have to be isolated to be used in synthesis, a renewed future for this ring system in preparative chemistry is predicted.

Acknowledgment. We thank the NIH and McNeil Pharmaceutical for supporting this study. A.B. (U. of Calcutta) visited Penn State as UNESCO Fellow in the UNDP Special Assistance to Selected Universities Program.

Registry No. **6a**, 90695-87-7; **6b**, 57439-39-1; **7a**, 90695-88-8; **7b**, 55401-03-1; **8a**, 90695-90-2; **8b**, 90695-92-4; **8c**, 90695-94-6; **8d**, 90695-95-7; **8e**, 90695-96-8; **8f**, 90695-98-0; **9a**, 90695-99-1; **9b**, 90696-00-7; **9c**, 90696-01-8; **9d**, 90696-02-9; **9e**, 90696-03-0; **11a**, 90696-04-1; **11b**, 90696-05-2; **11c**, 90696-06-3; **11d**, 90696-07-4.

Supplementary Material Available: Spectral data for new compounds (3 pages). Ordering information is given on any current masthead page.

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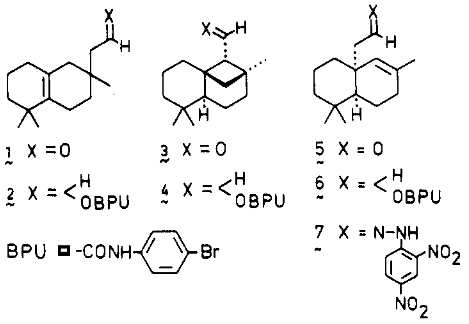
[13] Fourier transform NMR spectra were recorded on a Bruker Instruments WP-200 Spectrometer (50.32 MHz for ^{13}C). Coupling studies were used as an aid in making the spectral assignments.

[14] From reaction of **8f** with Cy$_2$NEt at −40 to +25 °C.

Acanthodoral and Isoacanthodoral, Two Sesquiterpenoids with New Carbon Skeletons from the Dorid Nudibranch *Acanthodoris nanaimoensis*

Summary: The structures of acanthodoral (**3**) and isoacanthodoral (**5**), two sesquiterpenoids with new carbon skeletons, have been solved by X-ray diffraction analysis of their (*p*-bromophenyl)urethane **4** and dinitrophenylhydrazone **7** derivatives, respectively.

Sir: We have recently reported that the extracts of the fragrant dorid *Acanthodoris nanaimoensis* contain three isomeric sesquiterpenoid aldehydes and we proposed a structure for the major component, nanaimoal (**1**).[1] In this paper we report the structures of the two minor sesquiterpenoid aldehydes. The extremely small quantities (7 mg of **3**, 40 mg **5**/100 animals) and high volatility of the minor components made the efficient isolation of either pure compound extremely difficult. We therefore isolated them as their (*p*-bromophenyl)urethane derivatives.



The least abundant component, acanthodoral (**3**), gave a crystalline (*p*-bromophenyl)urethane derivative **4**: mp 109–110 °C (hexane); MS, M$^+$, m/z 421, 419, C$_{22}$H$_{30}$BrNO$_2$; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.81 (s, 3 H), 0.89 (s, 3 H), 0.96 (s, 3 H), 1.09 (d, 1 H, J = 9.2 Hz), 1.84 (d, 1 H, J = 9.2 Hz), 4.14 (dd, 1 H, J = 11.1, 6.9 Hz), 4.17 (dd, 1 H, J = 11.1, 7.7 Hz), 6.50 (br s, 1 H), 7.27 (d, 2 H), 7.40 (d, 2 H). The remaining 12 protons appeared as a series of complex multiplets between δ 1.2 and 1.7. Since there were no known sesquiterpenoid carbon skeletons that could account for the observed spectral data, the structure of **4** was solved by a single-crystal X-ray diffraction analysis.

Crystals of **4** belonged to the common monoclinic space group $P2_1$ with a = 9.581 (1) Å, b = 6.406 (1) Å, c = 34.45 (1) Å, and β = 85.85 (1)°. Two molecules of composition C$_{22}$H$_{30}$O$_2$NBr formed the asymmetric unit. All unique diffraction maxima with $2\theta \lesssim 114°$ were collected on a computer-controlled four-circle diffractometer with a

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[1] Ayer, S. W.; Hellou, J.; Tischler, M.; Andersen, R. J. *Tetrahedron Lett.* **1984**, *25*, 141.

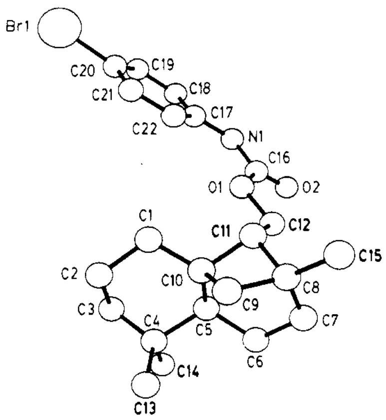


Figure 1.

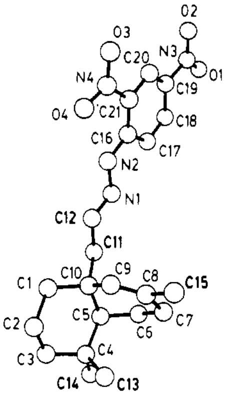
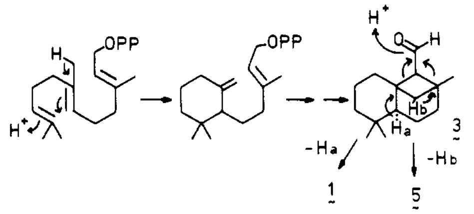


Figure 2.

Scheme I



variable 1° ω scan and graphite-monochromated Cu K$\bar{\alpha}$ radiation (1.54178 Å). After correction for Lorentz, polarization, and background effects, 2365 (75%) were judged observed $((|F_o| \gtrsim 3\sigma(F_o))$. A phasing model was found by standard heavy atom methods, and least-squares refinements with anisotropic heavy atoms and isotropic hydrogens have converged to a standard crystallographic residual of 0.078 for the observed reflections.[2] Both molecules in the asymmetric unit had the same stereostructure, and a computer-generated perspective drawing is given in Figure 1. Additional details can be found in the supplementary material section.

Isoacanthodoral (**5**), the second minor component, yielded the (*p*-bromophenyl)urethane derivative **6** as an oil: $[\alpha]_D$ −39° (hexane); MS, M$^+$, *m/z* 421, 419, $C_{22}H_{30}BrNO_2$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (s, 3 H), 1.01 (s, 3 H), 1.61 (br s, 3 H), 1.48 (ddd, 1 H, *J* = 13.0, 6.7, 8.9 Hz), 2.10 (ddd, 1 H, *J* = 13.0, 6.4, 9.0 Hz), 4.18 (m, 2 H), 5.06 (br s, 1 H), 6.50 (br s, 1 H), 7.27 (d, 2 H), 7.40 (d, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) (only terpenoid carbons are listed) δ 19.3, 20.0, 23.3, 26.5, 29.0, 32.3, 34.1, 37.5, 38.0, 40.4, 42.5, 45.6, 63.3, 131.0, 134.2.

In light of the already determined structures of nanaimoal (**1**) and acanthodoral (**3**), and spectral data, we proposed structure **6** for the urethane derivative of **5**. This was confirmed via a single-crystal X-ray diffraction analysis on the 2,4-dinitrophenylhydrazone **7**.[3] Crystals of **7** also belonged to space group $P2_1$ with *a* = 6.027 (1) Å, *b* = 31.613 (8) Å, *c* = 8.910 Å, and β = 80.89 (1)°. The asymmetric unit consisted of two molecules of composition $C_{21}H_{32}O_4N_4$. Diffraction data were collected by the method described above and 1713 (59%) were judged observed. Solution by direct methods was routine and least-squares refinements have converged to a standard crystallographic residual of 0.048.[2] A computer-generated perspective drawing of one of the identical molecules of **7** forming the asymmetric unit is given in Figure 2, and the supplementary material should be consulted for further details.

Acanthodoral (**3**) and isoacanthodoral (**5**) both have new sesquiterpenoid carbon skeletons for which we propose the names acanthodorane and isoacanthodorane. A proposed biogenesis for all three *A. nanaimoensis* sesquiterpenoids is shown in Scheme I.

Acknowledgment. We thank Mike Le Blanc and the staff of the Blamfield Marine Station for assistance in collecting *A. nanaimoensis*. Financial assistance from NSERC in the form of a grant to R.J.A. and a postgraduate scholarship to S.W.A. is acknowledged. The work at Cornell was supported by NIH CA24487 and NSF INT 8117327.

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, bond distances, and bond angles for 4 and 7 (14 pages). Ordering information is given on any current masthead page.

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[2] All crystallographic calculations were done on a PRIME 850 computer operated by the Cornell Chemistry Computing Facility. Principal programs employed were REDUCE and UNIQUE, data reduction programs by M. E. Leonowicz, Cornell University, 1978; MULTAN 78, a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data (locally modified to perform all Fourier calculations including Patterson syntheses) written by P. Main, S. E. Hull, L. Lessigner, G. Germain, J. P. Declercq, and M. M. Woolfson, University of York, England, 1978; BLS78A, an anisotropic block-diagonal least-squares refinement written by K. Hirotsu and E. Arnold, Cornell University, 1980; PLUTO78, a crystallographic illustration program by W. D. S. Motherwell, Cambridge Crystallographic Data Center, 1978; and BOND, a program to calculate molecular parameters and prepare tables written by K. Hirotsu, Cornell University, 1978.

[3] 2,4-Dinitrophenylhydrazone 7: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.90 (s, 3 H), 1.03 (s, 3 H), 1.66 (s, 3 H), 1.95 (m, 3 H), 2.24 (dd, *J* = 6.0, 14.0 Hz, 1 H), 2.79 (dd, *J* = 6.0, 14.0 Hz, 1 H), 5.11 (br s, 1 H), 7.42 (dd, *J* = 6.0, 6.0 Hz, 1 H), 7.88 (d, *J* = 9.4 Hz, 1 H), 8.25 (dd, *J* = 2.5, 9.4 Hz, 1 H), 9.08 (d, *J* = 2.5 Hz, 1 H), 10.9 (br s, 1 H), 1.1–1.8 (m, 8 H).

Aminyl Oxides (Nitroxides). 36.[1] Formation of 3,7-Dioxa-2,6-diazabicyclo[3.3.0]octanes by Dimerization of Vinyl Aminyl Oxides (Vinyl Nitroxides)

Summary: Oxidation of *N*-aryl-*N*-(2-aroyl-2-arylethyl)-hydroxylamines **5** yields dimers of the vinyl aminyl oxides

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[1] Aminyl oxides (nitroxides). 35, see; Aurich, H. G.; Baum, G.; Massa, W.; Mogendorf, K.-D.; Schmidt, M. *Chem. Ber.*, in press

0022-3263/84/1949-2654$01.50/0