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A VINYL CARBONIMIDIC DICHLORIDE FROM THE MARINE SPONGE PSEUDAXINYSSA PITYS

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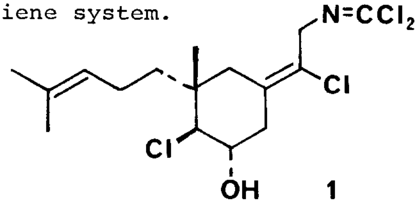
We have recently described the isolation and structural elucidation of two carbonimidic dichlorides 1 and 2 from the Indo-Pacific sponge *Pseudaxinyssa pitys*.[2] In this and the following paper[3] we wish to describe the structural elucidation of the minor metabolites of *P. pitys*. This paper describes the structural elucidation by single crystal X-ray diffraction analysis of a carbonimidic dichloride 3 in which the carbonimidic dichloride moiety is conjugated to a diene system.



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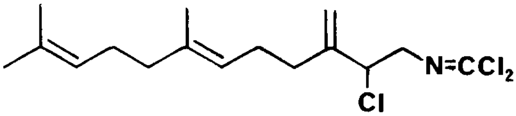

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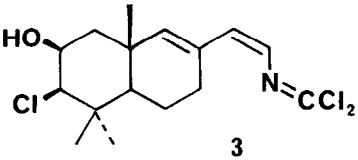

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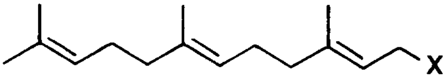


4 X = NCS
5 X = NC

The chloroform-soluble material from methanol extracts of P. pitys was chromatographed on silica gel, and selected fractions from that separation were rechromatographed by HPLC on μ-porasil to obtain the carbonimidic dichloride **3** (0.25% dry weight) as a crystalline solid, mp 171-2°C. The carbonimidic dichloride **3**, $C_{16}H_{22}NOCl_3$,[4] gave the following spectral data: $[\alpha]_D^{20}$ -15° (0.2, $CHCl_3$); uv (MeOH) 293 nm (10,000); ir (mull) 3550, 1630, 1575 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.08 (s, 3H), 1.11 (s, 3H), 1.25 (m, 1H), 1.27 (s, 3H), 1.46 (dd, 1H, J = 14, 2 Hz), 1.65 (m, 1H), 1.90 (m, 1H), 2.08 (dd, 1H, J = 14, 3 Hz), 2.46 (m, 1H, J = 18, 11, 7 Hz), 2.74 (dd, 1H, J = 18, 6 Hz), 3.82 (d, 1H, J = 3Hz), 4.12 (m, 1H, J = 2, 3, 3 Hz), 5.56 (s, 1H), 5.70 (d, 1H, J = 8 Hz), 6.38 (d, 1H, J = 8 Hz); ^{13}C nmr (CCl_4) δ 148.8 (d), 134.7 (d), 133.4 (s), 128.9 (d), 124.7 (s), 78.4 (d), 73.6 (d), 53.2 (d), 44.8 (t), 41.2 (s), 37.4 (s), 32.0 (q), 31.4 (t), 24.5 (q), 21.2 (t), 19.7 (q). The infrared and ultraviolet spectra suggested that the carbonimidic dichloride functionality was part of a conjugated chromophore containing a Z-disubstituted olefin and a trisubstituted olefin. We deduced that **3** was bicyclic and that it contained a vicinal chlorohydrin functionality. Since the carbonimidic dichloride **3** did not give a clean reaction with any reagent investigated, the structure was deduced by single crystal X-ray diffraction analysis.

Crystals of the carbonimidic dichloride **3** belong to the orthorhombic space group $P2_12_12_1$ with **a** = 5.908(5), **b** = 9.066(6) and **c** = 31.62(3)Å. An observed and calculated (z=4) density of ∿1.21 g/cc indicated that one molecule of $C_{16}H_{22}Cl_3NO$ formed the asymmetric unit. All unique diffraction maxima with $2\theta \leq 114.1°$ were collected on a four-circle diffractometer using graphite monochromated CuK (1.5418Å) radiation and a variable speed ω-scan. Of the 1378 reflections surveyed in this fashion, 1251 (91%) were judged observed [$I \geq 3\sigma(I)$] after correction for Lorentz, polarization, and background effects. A trial structure was arrived at, using a multisolution weighted tangent formula approach[5] and the tangent formula recycling procedure.[6] All twenty-one nonhydrogen atoms were located in this fashion. Most of the hydrogens were located on a ΔF_o-synthesis, but some were included at calculated positions. Full matrix least squares refinements, using anistropic temperature factors for the nonhydrogen atoms and fixed isotropic hydrogens and anomalous dispersion corrections for chlorine, have converged to a

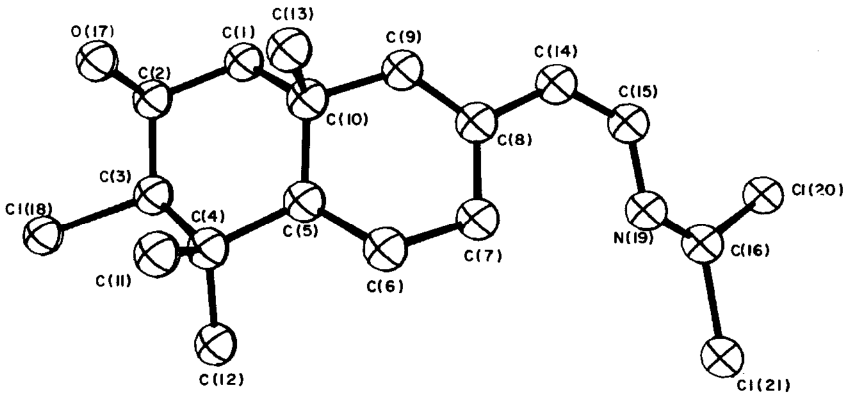
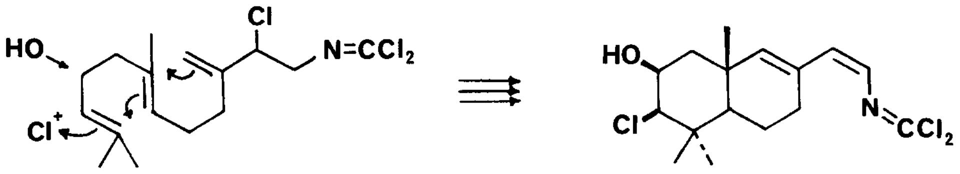


Figure 1. A computer-generated drawing of carbonimidic dichloride 3. Hydrogens are omitted for clarity, and the absolute configuration is that deduced from anomalous scattering of the chlorines.

standard crystallographic residual of 0.081 for the structure and 0.090 for the enantiomer.[7] Figure 1 shows a computer-generated perspective drawing of the final X-ray model. See the note on Supplemental Information[8] for further crystallographic details. In general, the metric details agree well with accepted values. The imidic dichloride has a C-Cl bond length of 1.73(1)Å, N=C bond length of 1.24(1), C-N bond length of 1.37(1) and C=C bond length of 1.33(1). The configurations are 2(S), 3(S), 5(R), 10(R) and 14(Z).

The carbon ring system of the carbonimidic dichloride 3 has not previously been reported among natural products.[9] The ring system can be envisaged as resulting from a "chloronium ion"-initiated cyclization of the acyclic metabolite 2 (or an equivalent molecule). The isolation of farnesyl isothiocyanate 4[10] (0.04% dry weight), but not farnesyl isonitrile 5, may provide a clue to the biosynthesis of the carbonimidic dichloride functionality.



Acknowledgements

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References and Notes

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4. Unlike compounds **1** and **2**, the conjugated carbonimidic dichlorides show a molecular ion.
5. The following library of crystallographic programs was employed: MULTAN, G. Germain, P. Main and M. M. Wolfson, *Acta Crystallogr.*, B26, 274 (1970 and references in M. M. Woolfson, *Acta Crystallogr.*, A33, 219 (1977); ORFLS (local version), W. R. Busing, K. O. Martin and H. A. Levy, Oak Ridge National Laboratory Report ORNL-TM-305; ORFFE, W. R. Busing and H. A. Levy, Oak Ridge National Laboratory Publication ORNL-59-12-3; ORTEP, C. K. Johnson, Oak Ridge National Laboratory Report ORNL-TM-3794.
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8. Tables of fractional coordinates, bond distances, bond angles and observed and calculated structure factors are available as a Supplement to this publication. To obtain a copy, contact the Photo Service, Iowa State University, Ames, Iowa 50011, requesting Supplement to Publication for this publication and submitting $.50 in the form of a check, cash, or money order Give name and complete address (including zip code) for mailing.
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