Tetrahedron Letters No. 16, pp 1395 - 1398, 1978. Pergamon Press. Printed in Great Britain.

# MINOR CARBONIMIDIC DICHLORIDES FROM THE MARINE SPONGE PSEUDAXINYSSA PITYS

Stephen J. Wratten and D. John Faulkner

Scripps Institution of Oceanography (A-012)
La Jolla, California 92093

(Received in USA 27 December 1978; received in UK for publication 6 March 1978)

In the previous paper,[1] we described the structural elucidation by single crystal X-ray diffraction analysis of a third carbonimidic dichloride **1** from the Indo-Pacific sponge Pseudaxinyssa pitys. From the same sponge we have isolated three minor metabolites, all of which contained the carbonimidic dichloride functionality. Although we have been unable to interconvert these molecules because of their instability under most reaction conditions, analysis of the spectral data has provided sufficient information to allow us to suggest the most likely structures. In this paper, we wish to report the structural elucidation from spectral data of three additional carbonimidic dichlorides.

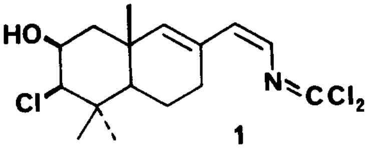
Selected fractions from a silica gel chromatography of the chloroform-soluble material from a methanolic extract of P. pitys were rechromatographed by HPLC on μ-porasil to obtain the carbonimidic dichlorides **1** (0.25% dry weight), **2** (0.08% dry weight), **3** (0.08% dry weight) and **4** (0.02% dry weight). Spin decoupling experiments allowed us to assign every signal in the $^1$H nmr spectrum of carbonimidic dichloride **1**. Similar decoupling experiments on the $^1$H nmr spectra of compounds **2** - **4** allowed most of the signals in each spectrum to be assigned (Table 1).

Carbonimidic dichloride **2** had the molecular formula $C_{16}H_{22}NOCl_3$, isomeric with **1**. The infrared, ultraviolet, and mass spectra of **2**[2] were almost identical to those of **1**.[1] In the $^1$H nmr spectra of **1** and **2**, the ring A proton signals are almost superimposable, while the differences in the spectra can all be reconciled by assuming that the $\Delta^{14,15}$ olefinic bond has the E geometry in **2**. This conclusion is supported by the 13 Hz coupling constant between the protons at C-14 and C-15 and by the larger extinction coefficient (22,000 vs. 10,000) in the ultraviolet spectrum.

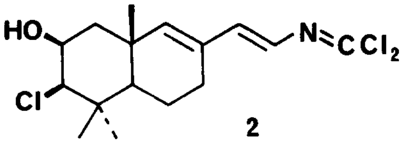
Carbonimidic dichloride **3**, $C_{16}H_{22}NOCl_3$, was also an isomer of **1**. Familiar signals in the infrared, ultraviolet, and mass spectra[3] again implied that **1** and **3** were closely related. The $^1$H nmr spectrum of **3** contained signals at $\delta$ 6.34 (d, 1H, J = 8 Hz) and 5.78 (d, 1H, J = 8 Hz) due to the Z-disubstituted olefinic bond in the side chain. The third olefinic proton signal at $\delta$ 5.91 (t, 1H, J = 5 Hz) was coupled to two protons, indicating the presence of a $\Delta^{7,8}$ olefinic bond. The two protons at C-9 appeared as an AB quartet at $\delta$ 2.46 (d, 1H, J = 17 Hz) and $\sim$2.1 (d, 1H, J = 17 Hz). Irradiation of the multiplet at 2.3 ppm caused both the triplet at 5.91 ppm and the signal at $\delta$ 1.39 (dd, 1H, J = 9, 7 Hz), assigned to the bridgehead proton at C-5, to become singlets, confirming the assignment of proton signals in ring B. The signals for protons in ring A were, again, almost superimposable on the corresponding signals in the spectrum of **1**. We observed signals that could be assigned to the expected fourth isomer having a $\Delta^{7,8}$, 14(E) diene system in a $^1$H nmr spectrum[4] of a partially purified sample, but this isomer decomposed during purification.

The remaining carbonimidic dichloride **4** was less polar than **1** - **3** and had the molecular formula $C_{16}H_{22}NCl_3$. The lack of a hydroxyl band in the infrared spectrum and the absence of a signal near 4.1 ppm in the $^1$H nmr spectrum implied that **4** was related to **1** by the absence of the hydroxyl group at C-2.[5] Using the arguments presented above, we assigned the position and geometry of the diene moiety on the basis of ultraviolet and $^1$H nmr data.

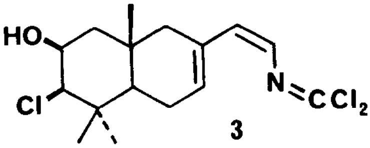
The coupling constants measured for the $^1$H nmr signal at $\delta$ 3.62 (dd, 1H, J = 11, 6 Hz) indicated that the chlorine at C-3 was equatorial. The chemical shifts of the signals due to the geminal methyl groups indicate the presence of halogen at C-3.



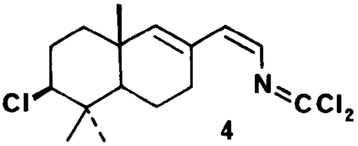
1



2



3



4

Table 1. $^{1}$H nmr spectra of compounds 1 - 4 in ppm from TMS (multiplicity, coupling constants)

| Proton at C#* | | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| 1 | ax | 1.46(dd,14,2) | 1.48(dd,14,2) | 1.48(dd,15,2) | --- |
| | eq | 2.08(dd,14,3) | 2.08(dd,14,3) | 2.21(dd,15,3) | --- |
| 2 | | 4.12(m,3,3,2) | 4.11(m,3,3,2) | 4.11(m,3,3,2) | --- |
| 3 | | 3.82(d,3) | 3.81(d,3) | 3.85(d,3) | 3.62(dd,11,6) |
| 5 | | 1.25(m) | 1.25(m) | 1.39(dd,9,7) | --- |
| 6 | | 1.90(m),1.65(m) | ∿1.8(m) | ∿2.3(m) | --- |
| 7 | ax | 2.46(m,18,11,7) | ∿2.2(m) | 5.91(t,5) | 2.40(m,18,12,7) |
| | eq | 2.74(dd,18,6) | 2.37(dd,18,6) | | 2.73(dd,18,7) |
| 9 | | 5.56(s) | 5.62(s) | 2.46(d,17)<br>∿2.1(d,17) | 5.49(s) |
| 11 | | 1.11(s) | 1.12(s) | 1.12(s) | 1.02 |
| 12 | | 1.08(s) | 1.08(s) | 1.03(s) | 0.91 |
| 13 | | 1.27(s) | 1.28(s) | 1.16(s) | 1.09 |
| 14 | | 5.70(d,8) | 6.43(d,13) | 5.78(d,8) | 5.70(d,8) |
| 15 | | 6.38(d,8) | 6.63(d,13) | 6.34(d,8) | 5.37(d,8) |

---

*See reference 1 for numbering system.

## Acknowledgements

We wish to thank Dr. Bill Stewart for the collection of P. *pitys*, which was identified by Ms. Linda Jones. Nmr spectra were obtained at the UCSD NMR Facility, supported by the National Institutes of Health (RR-708). This research was supported by grants from the National Institutes of Health (AI-11969) and the National Science Foundation (PCM-02539).

## References and Notes

1. S. J. Wratten, D. J. Faulkner, D. Van Engen and J. Clardy, *Tetrahedron Lett.*, 0000 (1978).

2. Ir ($CCl_4$) 3600, 1645, 1570 $cm^{-1}$; uv (MeOH) 288 (22,000); $^{13}C$ nmr ($CCl_4$) $\delta$ 146.7 (d), 137.8 (d), 129.7 (s), 128.9 (d), 76.6 (d), 72.0 (d), 51.6 (d), 42.8 (t), 39.4 (s), 35.5 (s), 30.1 (q), 26.1 (t), 22.5 (q), 18.8 (t), 17.8 (q); mass measurement 349.077, $C_{16}H_{22}NOCl_3$ requires 349.077.

3. Ir ($CCl_4$) 3600, 1640, 1580 $cm^{-1}$; uv (EtOH) 294 nm (11,000); $^{13}C$ nmr ($CDCl_3$) $\delta$ 133.7, 133.3, 132.6, 128.2, 126.6, 76.8, 72.3, 48.8, 48.5, 45.5, 39.0, 32.0, 30.0, 25.4, 20.6, 17.6; mass measurement 349.078, $C_{16}H_{22}NOCl_3$ requires 349.077.

4. Signals assigned to fourth isomer in crude $^1H$ nmr system: $\delta$ 6.68 (d, 1H, J = 13 Hz), 6.58 (d, 1H, J = 13 Hz), 5.99 (t, 1H, J = 5 Hz), 4.19 (m, 1H), 3.95 (1H, d, J = 3 Hz), 1.19 (s, 3H), 1.16 (s, 3H), 1.06 (s, 3H).

5. Ir ($CCl_4$) 1635, 1580 $cm^{-1}$; uv (MeOH) 293 (10,000); mass measurement 333.079, $C_{16}H_{22}NCl_3$ requires 333.082.