Tetrahedron Letters Vol. 21, pp 735-738
0040-4039/80/0215-0735$02.00/0

DEOXOSARCOPHINE FROM A SOFT CORAL, *SARCOPHYTON* SP.

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Abstract: A sample of deoxosarcophine (2) was converted into sarcophine (1) by autoxidation. Two reactions are described that will enable the enantiomers of deoxosarcophine to be interrelated.

The structure of sarcophine (1), a cembranoid from *Sarcophyton glaucum*, was determined by single crystal X-ray diffraction analysis[1] and the absolute configuration assigned from CD data.[2] The same soft coral was later shown to contain several related cembranoids, including two isomeric dihydrofurans having the spectral characteristics of stereoisomers of deoxosarcophine (2). Kashman[3] was unable to fully characterize these compounds but presented evidence to show that the dihydrofurans were epimers at C-2. Coll[4] has described an isomer of deoxosarcophine (2) from *Sarcophyton ehrenbergi* while Tursch[5] has reported, without details, an isomer of compound 2 from *S. trocheliophorum*. Selected physical data are compared in Table 1. We wish to report the correlation of our sample of deoxosarcophine (2) with sarcophine (1).

The soft coral *Sarcophyton* sp. was collected by SCUBA (-5m) from the leeward side of Canton Island (2°50'S, 171°40'W). Chromatography of dichloromethane soluble material on Florisil gave deoxosarcophine (2), m.p. 73°C, as the major metabolite (1.1% dry weight). Comparison of the spectral data[6] with those published by Kashman[3] convinced us that we had an isomer of deoxosarcophine (2). Exposure of a 5:1 dichloromethane-benzene solution of deoxosarcophine (2) to air under fluorescent lighting resulted in a smooth oxidation to obtain sarcophine (1) in 85% yield. Addition of a photosensitizer (methylene blue) caused rapid, destructive photooxidation. The spectral data of sarcophine (1), including the optical rotation and CD curve, isolated from photooxidation of 2 were identical to literature values.[1,2]

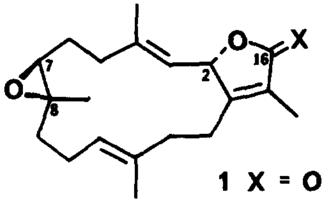
When deoxosarcophine was irradiated in the presence of oxygen and a catalytic amount of benzophenone in chloroform solution, an alcohol 3 was rapidly formed. The ^{1}H NMR spectrum[7] of 3 contained all the signals associated with the dihydrofuran ring together with signals at δ 5.07 (bs, 1H) and 4.90 (bs, 1H) due to an exocyclic methylene and at δ 4.17 (d, 1H, J = 10.5Hz) due to a secondary alcohol. This result indicated that the autoxidation of deoxosarcophine was highly dependent on the reaction conditions.

If the compounds reported by other workers are all isomers of deoxosarcophine, it should be possible to interrelate all isomers by using two chemical reactions together with spectral data. The geometry of the trisubstituted olefinic bonds and about the epoxide ring can be determined from the ^{13}C NMR chemical shifts of the methyl groups.[8] Assuming that the 7,8-epoxide is based on a trans-trisubstituted olefin, removal of the optical activity at C-2 leaves two possible optical enantiomers. Dehydrogenation of deoxosarcophine (2) over 10% palladium on charcoal in refluxing xylene gave the furan 4, $[\alpha]_D + 38^\circ$ (c = 0.5, $CHCl_3$), as an oil.[9] The relative configuration at C-2 can be determined by cleavage of the epoxide ring. Oxidation of deoxosarcophine (2) with periodic acid in dry ether at 25°C for 60 min. gave the keto-aldehyde 5, $[\alpha]_D + 56^\circ$ (c = 1.05 $CHCl_3$).[10] Both the furan 4 and the keto-aldehyde 5 were relatively unstable oils, with the furan being particularly unstable.

It is possible that the oxidation of deoxosarcophine (2) to sarcophine (1) is accompanied by epimerization at C-2, but until there is a need to explore that possibility, we prefer to accept that both compounds have the same absolute configurations at C-2, C-7 and C-8. This premise is supported

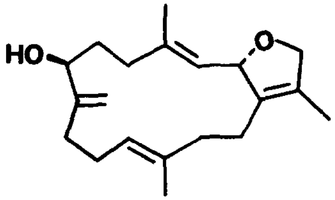
Table 1. Physical data for samples of deoxosarcophine.

Source	Location	mp	$[\alpha]_D$
Sarcophyton sp.	Canton Island	72-73°	+135°
S. ehrenbergi	Townsville	79-81°	-191°
S. trocheliophorum	Laing Island	oil	-137°
S. glaucum	Red Sea	oil	+ 40°



1 X = O

2 X = H_2



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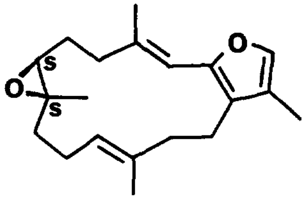

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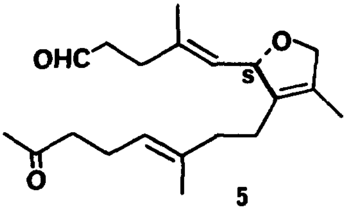

5

by the similar optical rotations of sarcophine (1) and deoxosarcophine (2).

Deoxosarcophine (2) has been shown to facilitate neuromuscular transmission in a rat diaphram.[11]

Acknowledgments

We thank Dr. A. Esser for providing CD measurements. This research was supported by the Sea Grant Program, Department of Commerce (04-6-158-44110) and by a fellowship from the National Research Council of Canada (to D.E.M.).

References and Notes

1. J. Bernstein, U. Shmeuli, E. Zadock and Y. Kashman, *Tetrahedron*, **30**, 2817 (1974).

2. Y. Kashman in "Marine Natural Products Chemistry," D. J. Faulkner and W. H. Fenical, Eds., Plenum, New York, 1977, p. 17.

3. Y. Kashman, E. Zadock and I. Néeman, *Tetrahedron*, **30**, 3615 (1974).

4. B. F. Bowden, J. C. Coll, W. Hicks, R. Kazlauskas and S. J. Mitchell, *Aust. J. Chem.*, **31**, 2707 (1978).

5. B. Tursch, *Pure Appl. Chem.*, **48**, 1 (1976).

6. mp 72-3^{o}; $[\alpha]_D$ + 135^{o} (c = 0.93, CHCl$_3$); IR (CHCl$_3$) 1675, 1450, 1380, 1250, 1050, 954, 760 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 1.20 (s, 3H), 1.58 (s, 3H), 1.63 (s, 3H), 1.80 (s, 3H), 2.52 (t, 1H, J = 4Hz), 4.35 (bs, 2H), 5.04 (dd, 1H, J = 5.5,9.5Hz), 5.12 (d, 1H, J = 10Hz), 5.36 (bd, 1H); ^{13}C NMR (CDCl$_3$) δ 138.9 (s), 136.5 (s), 133.2 (s), 127.7 (s), 126.2 (d), 123.6 (d), 83.6 (d), 78.2 (t), 61.7 (d), 59.6 (s), 39.6 (t), 37.5 (t), 36.5 (t), 25.9 (t), 25.2 (t), 23.4 (t), 16.8 (q), 15.4 (q), 15.0 (q), 10.0 (q).

7. ^{1}H NMR (CDCl$_3$) δ 1.59 (s, 3H), 1.65 (s, 3H), 1.82 (s, 3H), 4.17 (d, 1H, J = 10.5Hz), 4.51 (bs, 2H), 4.90 (s, 1H), 5.05 (t, 1H, J = 7Hz), 5.07 (s, 1H), 5.20 (d, 1H, J = 10Hz), 5.56 (bd, 1H, J = 10Hz).

8. G. E. Martin, J. A. Matson and A. J. Weinheimer, *Tetrahedron Lett.* 2195 (1979).

9. R$_f$ 0.43 (silica gel, 2:1 ether:hexane); IR (CCl$_4$ 1120 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 1.24 (s, 3H), 1.63 (s, 3H), 1.96 (s, 3H), 1.98 (s, 3H), 2.73 (t, 1H, J = 7Hz), 5.00 (m, 1H), 5.89 (s, 1H), 6.94 (s, 1H).

10. R$_f$ 0.30 (silica gel, ether); IR (CCl$_4$) 1730, 1040 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 1.60 (s, 6H), 1.75 (s, 3H), 2.05 (s, 3H), 4.34 (bs, 2H), 5.00 (m, 2H), 5.21 (m, 1H), 9.70 (s, 1H).

11. R. Jacobs, personal communication.

(Received in USA 13 September 1979)