7-Dehydrosarcophytin, another Novel Diterpenoid from the Soft Coral *Sarcophyton elegans* of the Indian Ocean†

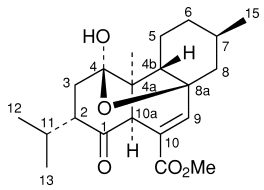
J. Chem. Research (S), 1999, 140–141†

Ammanamanchi S. R. Anjaneyulu,* Ponnapalli M. Gowri and Moturu V. R. Krishna Murthy

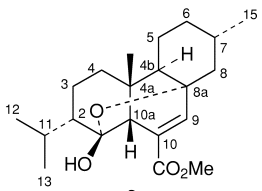
Department of Organic Chemistry, School of Chemistry, Andhra University, Visakhapatnam 530 003, India

7-Dehydrosarcophytin (**3**), another novel diterpenoid, has been isolated from the Indian Ocean soft coral *Sarcophyton elegans*, in addition to sarcophytin, and its structure elucidated using spectral data.

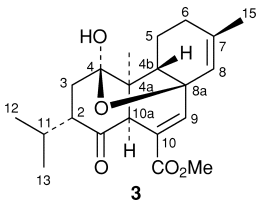
Chemical examination of the soft coral species *Sarcophyton elegans* occurring in different regions of the Pacific Ocean has been reported to yield polyhydroxy steroids[1–3] and cembranoid diterpenoids.[4] From the same species, collected from the Havelock (12°19′N, 93°48′E) Island of the Andaman and Nicobar group of Islands of the Indian Ocean, we have recently reported the isolation of a novel tetracyclic diterpenoid, named sarcophytin (**1**) and its structure elucidation by spectral data and X-ray analysis.[5] Sarcophytin (**1**) is the second example of this new class of diterpenes that bear a perhydrophenanthrene skeleton with an additional hemiketal ring; the other compound is chatancin[6] (**2**). Further examination of the ethyl acetate extract of the same species resulted in the isolation a new member of this series whose structure has been established as 7-dehydrosarcophytin (**3**) by a study of its physical and spectral (^{1}H, ^{13}C NMR, 2D NMR (^{1}H–^{1}H, ^{1}H–^{13}C COSY, ^{1}H–^{1}H NOESY), mass) data.



1



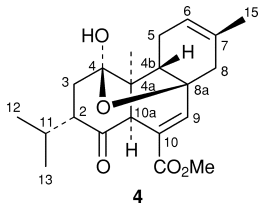
2



3

7-Dehydrosarcophytin (**3**) obtained from the hexane:ethyl acetate (8:2) eluent of the ethyl acetate extract over a silica gel column came as colourless needles; mp 160–162 °C, 80 mg, $[\alpha]_D^{30}$ +403.6° (*c* 0.5, $CHCl_3$), analysed for $C_{21}H_{28}O_5$ by elemental analysis and M^+ 360 in its EIMS. Its spectral characteristics, UV, IR and ^{1}H NMR, closely resembled those of sarcophytin (**1**); for example, through the presence of an hydroxylic absorption (3410 cm^{-1}), two carbonyls, a six-membered saturated ketone (1714 cm^{-1}) and an α,β-unsaturated ester (1683 cm^{-1}), and the UV absorption at 220 nm indicative of conjugation. Like sarcophytin (**1**), it exhibited a tertiary methyl (δ 1.11, s, 14-H_3), an isopropyl group (δ 0.81, d, $J = 6.3$ Hz, 12 and 13-H_3, δ 1.90, m), a carbomethoxyl (δ 3.71, s) and a β-proton of an α,β-unsaturated ester (δ 6.98, s). But, unlike **1**, instead of a secondary methyl, a methyl on a trisubstituted double bond was observed as a singlet at δ 1.75, with the olefinic proton appearing at δ 5.36 as a clear singlet. The foregoing evidence suggests that the new compound might be dehydrosarcophytin (**3**).

The new diterpene exhibited all the expected 21 carbon signals, which were analysed by its DEPT spectrum as five methyls, three methylenes, six methines and seven quaternary carbons. The chemical shifts of the respective carbons were assigned, based on the connectivities noticed in its 2D NMR (^{1}H–^{13}C COSY spectrum, Table 1). The presence of an oxygenated carbon at δ 105.6, assignable to a hemiketal carbon in a five-membered ring as in sarcophytin (**1**) unlike in chatancin which has a six-membered hemiketal ring appearing at δ 99.9, revealed the identity of the basic skeleton. The two carbonyl functionalities, the keto (δ 210.2) and the ester carbonyl (δ 165.6), and the two olefinic carbons of a trisubstituted double bond observed at δ 145.9 and δ 131.7 are as found in **1**. The additional double bond in the new dehydroderivative (**3**) was indicated by the olefinic carbons at δ 131.1 and 121.4.



4

Thus the new diterpene is dehydrosarcophytin, which might possess either of the alternative structures: a 7-dehydro-derivative (**3**) or a 6-dehydro-derivative (**4**). If it were a 6-dehydro-derivative, the trisubstituted olefinic 6-H should appear as a doublet/doublet, a triplet or, at least, as a doublet when one of the vicinal methylene protons at C-5 makes a dihedral angle of 90°. On the other hand, if it were a 7-dehydro-derivative the 8-H would appear as a singlet in the absence of vicinal protons. The appearance of this olefinic proton in **3** at δ 5.36 as a clear singlet, even in 300 MHz spectrum, was taken to support the structure of new diterpene as 7-dehydrosarcophytin (**3**). In addition, the same proton neither exhibited ^{1}H–^{1}H COSY nor NOESY connectivity with any protons except for the allylic connectivity with 15-H_3 which further supports its 7-dehydro structure. The ^{13}C values of the new diterpene (Table 1) agreed very closely with those of sarcophytin (**1**), except for the carbons C_{4b}, C_5 and C_6 where the deviation might be expected to be owing to the quasi chair form of ring C in the new compound with a double bond. In view of their closeness in ^{13}C values, the relative stereochemistry of 7-dehydrosarcophytin (**3**) was taken to be as in sarcophytin, whose structure was determined by X-ray analysis. This was also supported by the following partial connec-

*To receive any correspondence.

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 NMR spectral data of 7-dehydrosarcophytin (**3**), sarcophytin (**1**) and chatancin (**2**)

Carbon no.	δ_C			δ_H		^1H–^{13}C COSY	^1H–^1H COSY	^1H–^1H NOESY
	1[a]	**2**[b]	**3**[a]	**1**[c]	**3**[c]	**3**[c]	**3**[c]	**3**[c]
1	209.9 (s)	99.9	210.2 (s)					
2	56.0 (d)	50.8	55.5 (d)	2.10 (m)	2.05 (m)	2-H-C_2	12-H_3, 13-H_3	12-H_3, 13-H_3, 3-H
3	40.9 (t)	19.3	40.4 (t)	2.35 and 1.85 (m)	2.45 and 1.85 (m)	3-H-C_3	2-H	2-H
4	105.6 (s)	30.0	105.6 (s)					
4a	51.9 (s)	37.3	50.9 (s)					
4b	48.7 (d)	49.1	44.7 (d)	2.45 (m)	2.45 (m)	4b-H-C_{4b}	5-H	
5	21.3 (t)	28.5	23.1 (t)	1.45 (m)	1.64 (m)	5-H-C_5	6-H	
6	33.8 (t)	360	41.1 (t)	1.66 (m)	2.4 (1H, m) and 1.8 (1H, m)		15-H_3	15-H_3
7	29.9 (d)	30.9	131.1 (s)					
8	43.7 (t)	43.5	121.4 (d)	2.10 (m)	5.36 (br s)	8-H-C_8	15-H_3	
8a	79.3 (s)	77.0	77.6 (s)					
9	145.9 (d)	144.5	145.9 (d)	7.10 (s)	6.98 (s)	9-H-C_9	10a-H, 14-H_3	10a-H
10	130.9 (s)	137.0	131.7 (s)					
10a	49.8 (d)	54.4	48.5 (d)	2.98 (d, 2)	3.11 (s)			9-H, 14-H_3
11	25.9 (d)	26.4	25.6 (d)		1.90 (m)			
12	19.0 (q)	18.7	18.8 (q)	0.84 (d, 6)	0.81 (d, 6.3)	12-H_3-C_{12}	12-H_3, 13-H_3, 2H	
13	21.3 (q)	23.5	21.0 (q)	0.84 (d, 6)	0.83 (d, 6.3)	13-H_3-C_{13}	11-H	
14	16.8 (q)	24.4	16.8 (q)	1.10 (s)	1.11 (s)	14-H_3-C_{14}	11-H	10a-H
15	22.2 (q)	22.8	23.8 (q)	1.06 (d, 5.5)	1.75 (s)			6-H
16	165.9 (s)	167.2	165.6 (s)					
17	51.3 (q)	52.8	51.7 (q)	3.73 (s)	3.71 (s) 3.4 (s, OH)	17-H_3-C_{17}		10a-H 3-H

[a]Spectra recorded at 22.5 MHz in $CDCl_3$ with Me_4Si as reference. [b]From Ref. 6. [c]Spectra recorded at 90 MHz in $CDCl_3$ with Me_4Si as reference.

tivities in its NOESY spectrum (Table 1). For example, 10a-H exhibited connectivity with 14-H_3, indicating their *cis* relationship, and to 9-H, showing allylic coupling. The same proton did not exhibit coupling with 2-H, showing their *trans* relationship. Similarly, the absence of a NOESY connectivity between 14-H_3 and 4b-H again showed their *trans* relationship.

The structure and relative stereochemistry of the new diterpene could thus be fixed as 7-dehydrosarcophytin **3** which is only the third member of this class of diterpenes.

Experimental

Extraction and isolation of compounds **1** *and* **3**: the soft coral *Sarcophyton elegans* (3.2 kg, wet weight) was collected from Havelock Island of the Andaman and Nicobar group of Islands of the Indian Ocean in April 1994. It was dried, sliced into small pieces and boiled under reflux with methanol (8 × 5 L). The concentrated aqueous methanolic extract was fractionated into ethyl acetate. The ethyl acetate extract (20 g) was dried over anhydrous magnesium sulfate, concentrated and the residue was subjected to vacuum liquid chromatography[7] over a column of silica gel (230 g, 230–400 mesh) using a gradient of solvent mixtures from light petroleum to ethyl acetate. Elution with a mixture of light petroleum:ethyl acetate (8:2) gave a mixture of **1** and **3**. This mixture was separated over a small column of silica gel to furnish sarcophytin (**1**): 60 mg, mp 162–163 °C; $[\alpha]_D^{30}$ +924.4° (*c*, 0.5 $CHCl_3$); ν_{max}/cm^{-1} 3520, 1708 and 1720; λ_{max}/nm 219 (Found C, 69.8; H, 8.1. $C_{21}H_{30}O_5$ requires C, 69.6; H, 8.3%); EIMS, 362 (M^+); and 7-dehydrosarcophytin (**3**), 80 mg, mp 160–162 °C; $[\alpha]_D^{30}$ +403.6° (*c* 0.5, $CHCl_3$); ν_{max}/cm^{-1} 1714, 1683, 1450, 1366, 1277, 1245, 1205, 1109 and 750; λ_{max}/nm 220 (Found C, 70.2; H, 7.7. $C_{21}H_{28}O_5$ requires C, 70.0; H, 7.8%); EIMS, 360 (M^+).

Techniques Used.—Polarimetry, IR, UV, ^1H and ^{13}C NMR, including 2D NMR (^1H–^1H, ^1H–^{13}C COSY and ^1H–^1H NOESY), and EIMS.

We are grateful to the Department of Ocean Development, New Delhi for financial support and to the CSIR for sanctioning an Emeritus Scientist Scheme to the senior author (ASRA).

Received, 8th September 1998; Accepted, 20th October 1998
Paper E/8/06980H

References

1 J. M. Maldowan, B. Tursh and C. Djerassi, *Steroids*, 1974, **24**, 387.
2 A. Kanozawa, S. Teshima, T. Ando and S. Tomita, *Nippon Suisan Gakkaishing*, 1974, **40**, 729.
3 J. M. Maldowan, W. L. Tan and C. Djerassi, *Steroids*, 1975, **26**, 107.
4 Y. Uchio, M. Nitta, H. Nozaki, M. Nakayama, T. Iwagawa and T. Hase, *Chem. Lett*., 1983, 1719.
5 A. S. R. Anjaneyulu, M. J. R. V. Venugopal, P. Sarada, G. V. Rao, J. Clardy and E. Lobkovsky, *Tetrahedron Lett*., 1998, **39**, 135.
6 M. Sugano, T. Shindo, A. Sato, Y. Iijima, T. Oshima, H. Kuwano and T. Hata, *J. Org. Chem*., 1990, **55**, 5803.
7 J. C. Coll and B. F. Bowden, *J. Nat. Prod*., 1986, **49**, 934.