

ALCYONOLIDE, A NOVEL DITERPENOID FROM A SOFT CORAL

Motomasa Kobayashi,^{a)} Tohru Yasuzawa,^{a)} Yuji Kobayashi,^{b)}
Yoshimasa Kyogoku,^{b)} and Isao Kitagawa^{a)}*

a) Faculty of Pharmaceutical Sciences, Osaka University,
1-6, Yamada-oka, Suita, Osaka 565, Japan

b) Institute for Protein Research, Osaka University,
3-2, Yamada-oka, Suita, Osaka 565, Japan

Summary: A novel diterpenoid acetate named alcyonolide has been isolated from an Okinawan soft coral of the genus Alcyonium and the absolute stereostructure 1 has been assigned on the basis of chemical and physicochemical evidence.

During the course of study on marine natural products,¹⁾ we have isolated a new diterpenoid acetate named alcyonolide having a novel carbon framework from an Okinawan soft coral of the genus Alcyonium (an unidentified sp.). This paper deals with evidence being consistent with the absolute stereostructure 1 for alcyonolide.

The acetone extract prepared below 30° of the fresh soft coral was partitioned into AcOEt-water. Silica gel column chromatography of the AcOEt soluble portion gave alcyonolide (1), colorless oil, $[\alpha]_D^{24} -20^\circ$ (CHCl₃), EI-MS(m/z): 390 (M⁺, C₂₂H₃₀O₆²), 330 (M⁺-AcOH, C₂₀H₂₆O₄), 321 (M⁺-C₅H₉, C₁₇H₂₁O₆), 279 (M⁺-C₇H₁₁O, C₁₅H₁₉O₅, base peak), 219 (M⁺-C₇H₁₁O-AcOH, C₁₃H₁₅O₃), UV (MeOH): transparent above 210 nm, IR (CCl₄, cm⁻¹): 1738, 1720 (CO), 1673 (-C=C-O-), in 0.7% yield from the fresh animal. Treatment of the AcOEt soluble portion with n-BuOH (40-50°) followed by column chromatography furnished a secondary product 2, C₂₆H₄₀O₇,³⁾ colorless oil, $[\alpha]_D^{24} +64^\circ$ (CHCl₃), CI-MS (NH₃): 482 (M+NH₄)⁺, EI-MS: 446 (M⁺-H₂O, C₂₆H₃₈O₆), 386 (M⁺-H₂O-AcOH, C₂₄H₃₄O₄), IR (CCl₄): 3500(OH), 1732 (CO), 1669 (-C=C-O-).

PCC oxidation⁴⁾ of 2 yielded an enone (3) together with a minor dialdehydic derivative (4) (unstable). 3, colorless oil, $[\alpha]_D^{25} +141^\circ$ (CHCl₃), EI-MS: 462 (M⁺, C₂₆H₃₈O₇), UV (MeOH, nm, ε): 242 (10400), IR (CCl₄): 1729 (br, CO),

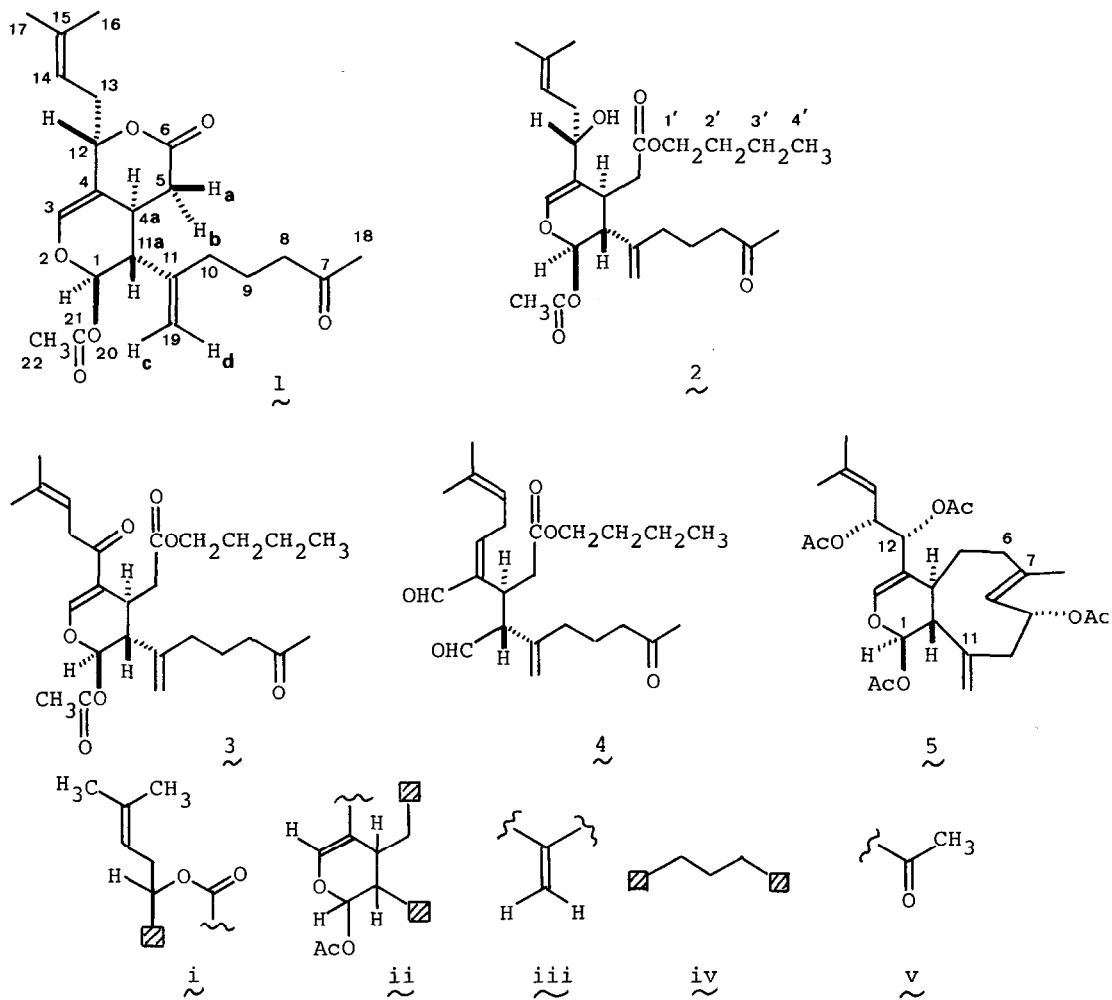


Fig. 1 (▨ : a quaternary carbon)

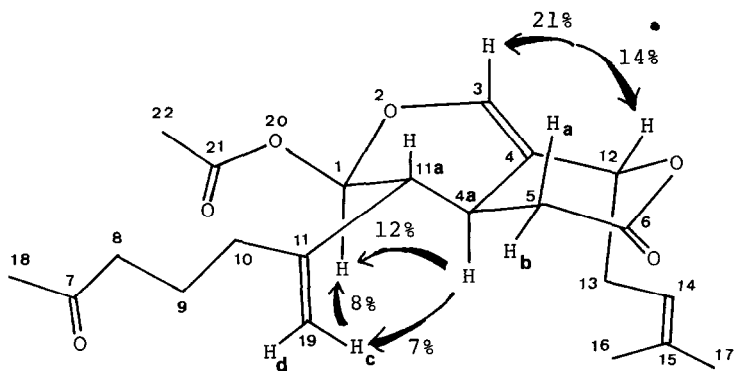


Fig. 2

Table I ^1H NMR data for 1, 2, 3 and 4 (CDCl_3)

H	<u>1</u> (360 MHz)	<u>2</u> (200 MHz)	<u>3</u> (200 MHz)	<u>4</u> (200 MHz)
1	5.96 (d, J=7.5)	6.11 (d, J=2.4)	6.29 (deformed dd, J=1.5, 1.5)	9.26 (d, J=2.4)
3	6.41 (s)	6.35 (s)	7.47 (s)	9.24 (d, J=2.0) ⁵⁾
4a	2.77 (m)	2.93 (t, J=10.7)	3.13 (br. t, J=7.8)	3.60 (m)
5a	2.32 (dd, J=18.5, 12.5)	2.80 (d, J=10.7)	2.69 (d, J=7.8)	2.75 (dd, J=15.6, 10.7)
5b	2.76 (dd, J=18.5, 6.0)			2.48 (dd, J=15.6, 3.4)
8	2.48 (t, J=7)	2.45 (t, J=6.8)	2.45 (t, J=7.3)	2.46 (t, J=7.1)
9	1.74 (qui., J=7)	1.7 (m)	1.7 (m)	1.7 (m)
10	2.07, 2.97 (dd, ABq, J=7, 7, 14.5)	2.1 (m)	2.1 (m)	2.0 (m)
12	4.79 (t, J=7.5)	4.06 (t, J=6.4)		6.53 (t, J=7.3)
13	2.46, 2.54 (dd, ABq, J=7.5, 7.5, 14)	2.21 (m)	3.27 (d, J=6.8)	3.26, 3.32 (dd, ABq, J=7.3, 7.3, 14)
14	5.11 (t, J=7.5)	5.04 (t-like, J=6.3)	5.28 (br. t, J=6.8)	5.18 (m)
16 } 17 }	1.61, 1.73 (both s)	1.64, 1.71 (both s)	1.64, 1.74 (both s)	1.72, 1.75 (both s)
18	2.15 (s)	2.14 (s)	2.14 (s)	2.15 (s)
19c	4.94 (s)	4.95 (s)	4.83 (s)	5.14 (s)
19d	5.04 (s)	4.90 (s)	4.87 (s)	5.25 (s)
22	2.11 (s)	2.11 (s)	2.13 (s)	
1'		4.10 (t, J=6.8)	4.08 (t, J=6.4)	3.94, 4.10 (t, ABq, J=6.6, 10.8)
2'		1.61 (m)	1.61 (m)	1.54 (m)
3'		1.37 (m)	1.37 (m)	1.32 (m)
4'		0.94 (t, J=7.1)	0.93 (t, J=7.1)	0.90 (t, J=7.3)

Table II ^{13}C NMR data for 1, 2, 3 and 4 (CDCl_3)

C	<u>1</u> (50 MHz)	<u>2</u> (50 MHz)	<u>3</u> (25 MHz)	<u>4</u> (25 MHz)
1	92.7 (d)	92.0 (d)	91.6 (d)	195.1 (d)
3	137.5 (d)	138.6 (d)	152.5 (d)	198.1 (d)
4	110.3 (s)	116.0 (s)	118.1 (s)	140.4 (s)
4a	31.1 (d) ^{a), b)}	30.0 (d)	30.0 (d)	33.0 (d)
5	34.9 (t) ^{a)}	33.8 (t)	28.0 (t)	28.7 (t)
6	169.7 (s) ^{a)}	173.0 (s)	172.2 (s)	172.3 (s)
7	207.9 (s)	208.6 (s)	208.6 (s)	208.1 (s)
8	42.6 (t)	42.9 (t)	42.8 (t)	42.8 (t)
9	21.4 (t) ^{a)}	21.6 (t)	21.6 (t)	21.1 (t)
10	34.7 (t) ^{a)}	34.9 (t)	34.7 (t)	34.8 (t) ^{a)}
11	145.0 (s)	146.1 (s)	145.8 (s)	141.7 (s)
11a	48.5 (d)	43.5 (d)	41.5 (d)	60.3 (d)
12	79.2 (d)	72.8 (d)	169.7 (s)	159.9 (d)
13	34.9 (t) ^{a), b)}	38.5 (t)	37.2 (t)	34.5 (t) ^{a)}
14	117.9 (d)	119.8 (d)	116.7 (d)	119.2 (d)
15	135.5 (s)	134.8 (s)	135.2 (s)	134.8 (s)
16	18.1 (q)	18.1 (q)	18.1 (q)	18.0 (q)
17	25.7 (q)	25.9 (q)	25.7 (q)	25.7 (q)
18	29.9 (q)	30.1 (q)	30.0 (q)	30.0 (q)
19	113.4 (t)	112.0 (t)	111.8 (t)	116.6 (t)
21	169.0 (s) ^{a)}	169.4 (s)	168.9 (s)	
22	20.7 (q)	21.1 (q)	21.0 (q)	
1'		64.4 (t)	64.4 (t)	64.4 (t)
2'		30.7 (t)	30.7 (t)	30.6 (t)
3'		19.2 (t)	19.1 (t)	19.1 (t)
4'		13.7 (q)	13.7 (q)	13.6 (q)

a) The assignments are interexchangeable. b) The two-carbon intensity of overlapping signal was confirmed by the hetero-decoupling without NOE method.

1671, 1639 (-C=C-CO-). 4, colorless oil, $[\alpha]_D^{25} -35^\circ$ (CHCl₃), CI-MS (NH₃): 422 (M+NH₄)⁺, UV (MeOH): 222 (11400), IR (CCl₄): 2715 (CHO), 1721 (br, CO), 1681, 1628 (-C=C-CHO).

The detailed ¹H NMR examinations of 1, 2, 3, and 4 including decoupling experiments (Table I) together with the ¹³C NMR (Table II) and MS examinations have shown the presence of partial structures i, ii, iii, iv, and v in alcyonolide. The long-range coupling observed between 3-H⁶⁾ and 4a-H in 4 (J= 2.4 Hz), 1-H and 4a-H in 3, and 10-H₂ and 19-H_d in 1, 2, 3, and 4 have led us to combine these partial structures into the carbon framework of alcyonolide (1).

In regard to the configurations at C-1, C-4a, C-11a, C-12 of 1, the ¹H NMR signal patterns (Table I) and the NOE examinations of alcyonolide (1) (Fig. 2) have defined the relative stereochemistry. Finally, the absolute stereostructure of alcyonolide (1) has been clarified on the basis of the Horeau's method⁷⁾ applied to 2 which has defined C-12 of 1 to be S.⁸⁾

The carbon framework of alcyonolide (1) corresponds to a seco-type variety of xenicin (5),⁹⁾ which was isolated from the Australian soft coral Xenia elongata. The biogenetic pathway of alcyonolide (1) is presumed to proceed after completion of a xenicin-type carbon framework.⁹⁾

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References and Notes

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