Communications to the Editor

[Chem. Pharm. Bull. 31(4)1440—1443(1983)]

ABSOLUTE STEREOSTRUCTURES OF CLAVIRIDENONE-A, -B, -C, AND -D FOUR PROSTANOIDS FROM THE OKINAWAN SOFT CORAL CLAVULARIA VIRIDIS

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By means of the circular dichroic exciton chirality method applied to various benzoyl derivatives, the absolute stereostructures of claviridenone-a (1), -b (2), -c (3), and -d (4), which were isolated from the Okinawan soft coral *Clavularia viridis*, have been elucidated.

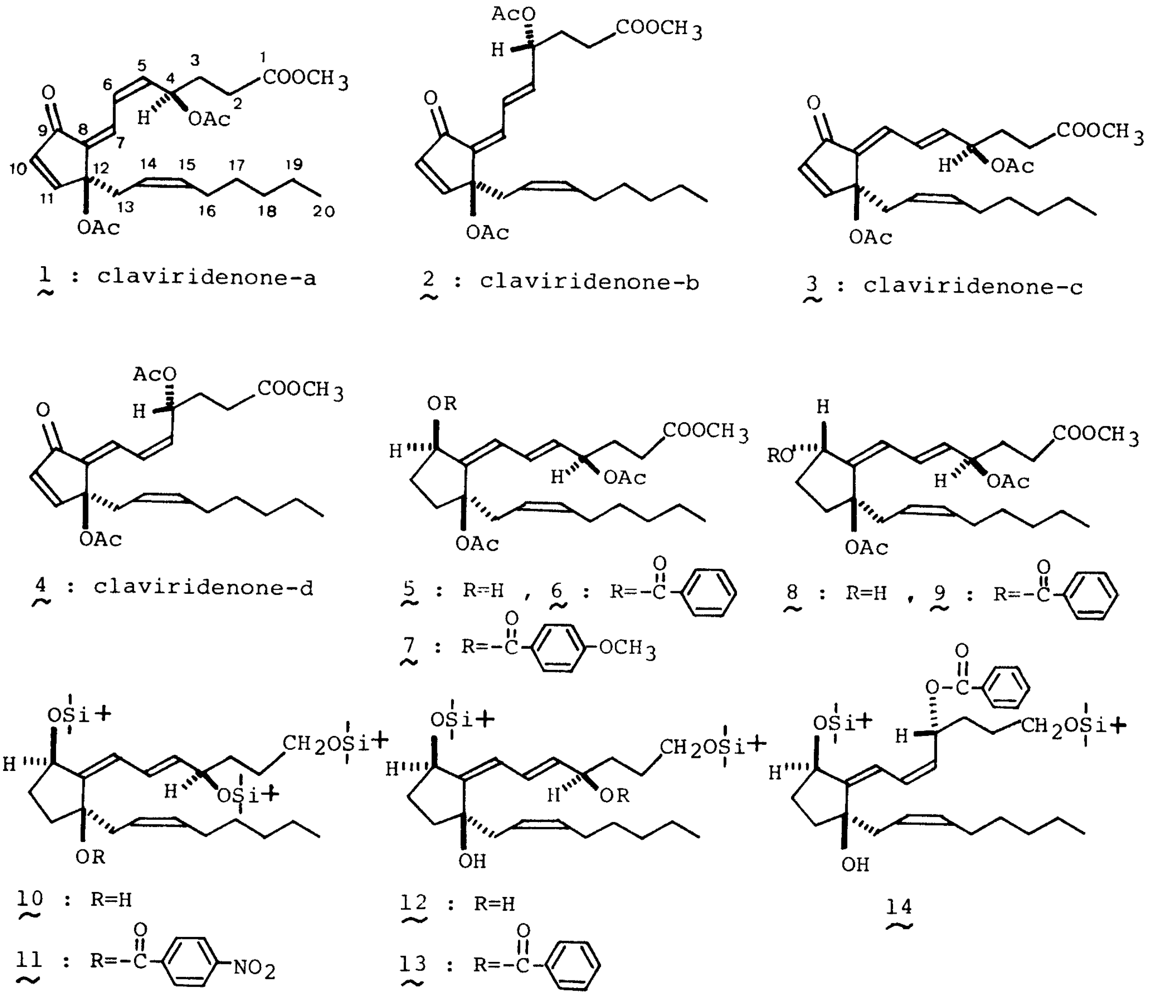
KEYWORDS —— claviridenone; prostanoid; soft coral; *Clavularia viridis*; Clavulariidae; CD; exciton chirality method; ^{13}C NMR

As a continuing study on marine natural products,1) we reported the plane structures of four new prostanoids named claviridenone-a (1), -b (2), -c (3), and -d (4), which were isolated from the Okinawan soft coral *Clavularia viridis* Quoy and Gaimard (Stolonifera, Clavulariidae).2) We have now elucidated the absolute stereostructures of these prostanoids by means of an extension of the CD exciton chirality method,3) which is the subject of this communication.

As reported previously,2) claviridenone-a (1), -b (2), -c (3), and -d (4) are geometric isomers in regard to the 5,7-diene chromophores in their α-chains and possess the same but unknown C-4 and C-12 absolute configurations. In order to investigate this matter, we prepared some benzoylated analogs from claviridenone-c (3) and -d (4) and have examined them by use of the CD exciton chirality method.3)

NaBH$_4$ reduction of claviridenone-c (3) yielded two tetrahydro isomers, 5 2,4) and 8, $C_{25}H_{38}O_7$,5) λ_{max}^{MeOH} 251 nm (ε 22000), in 10:1 ratio. Benzoylation of 5 and 8 furnished respective monobenzoates, 6 and 9, both $C_{32}H_{42}O_8$. The CD spectra of both monobenzoates demonstrated occurrence of the coupling between CD excitons of the 5,7-diene and the C-9 benzoyloxy chromophores, respectively (Table I). From signs of the first Cotton effect, the C-9 configurations in 6 and 9 have been assigned R and S, respectively, as depicted in Fig. 1. In the case of the anisoyl derivative (7) of 5, $C_{33}H_{44}O_9$, an enhanced Cotton effect was observed in the CD spectrum (Table I), which is attributable to an overlap of the UV absorption maxima of the anisoyl and the 5,7-diene chromophores.3)

Since a Cotton effect, resulting from the coupling between the conjugated diene and the allylic benzoate excitons, has been observed, we next prepared the C-4 and the C-12 benzoates in order to elucidate the absolute configurations at C-4 and C-12. LiAlH$_4$ reduction followed by *t*-butyldimethylsilylation of 5 furnished a



1 : claviridenone-a

2 : claviridenone-b

3 : claviridenone-c

4 : claviridenone-d

5 : R=H , 6 : R=$-\mathrm{C}(=\mathrm{O})-\mathrm{C_6H_5}$

7 : R=$-\mathrm{C}(=\mathrm{O})-\mathrm{C_6H_4}-\mathrm{OCH_3}$

8 : R=H , 9 : R=$-\mathrm{C}(=\mathrm{O})-\mathrm{C_6H_5}$

10 : R=H

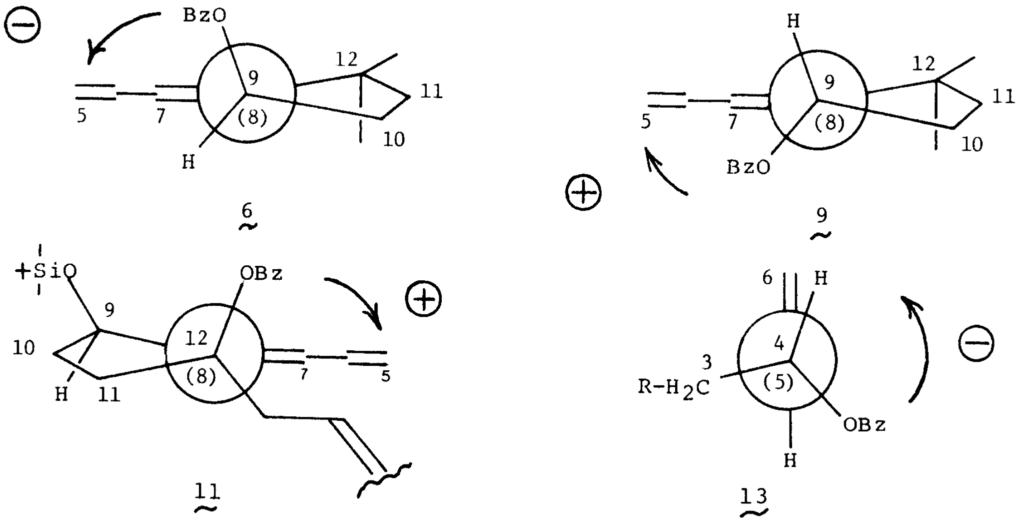
11 : R=$-\mathrm{C}(=\mathrm{O})-\mathrm{C_6H_4}-\mathrm{NO_2}$

12 : R=H

13 : R=$-\mathrm{C}(=\mathrm{O})-\mathrm{C_6H_5}$

14

Chart 1



6

9

11

13

Fig. 1

Table I. UV and CD Data for 6, 7, 9, 11, 13, and 14

	UV λ_{max} (MeOH)	CD (MeOH)
6	229 nm (ε=25000)	$[\theta]_{295}$ 0 , $[\theta]_{246}$ -95000 (neg.max.) , $[\theta]_{232}$ 0 ,
	245 nm (sh. ε=20000)	$[\theta]_{225}$ +37000 (pos.max.) , $[\theta]_{211}$ +13000 (pos.min.) , $[\theta]_{200}$ +76000!
7	249 nm (ε=36000)	$[\theta]_{290}$ 0 , $[\theta]_{262}$ -159000 (neg.max.) , $[\theta]_{249}$ 0 ,
		$[\theta]_{241}$ +69000 (pos.max.) , $[\theta]_{224}$ +6000 (pos.min.) , $[\theta]_{200}$ +58000!
9	242 nm (ε=25000)	$[\theta]_{286}$ 0 , $[\theta]_{245}$ +64000 (pos.max.) , $[\theta]_{237}$ 0 ,
		$[\theta]_{228}$ -79000 (neg.max.) , $[\theta]_{214}$ 0 , $[\theta]_{207}$ +22000 (pos.max.)
11	247 nm (ε=37000)	$[\theta]_{310}$ 0 , $[\theta]_{265}$ +30000 (pos.max.) , $[\theta]_{257}$ 0 ,
		$[\theta]_{240}$ -85000 (neg.max.) , $[\theta]_{216}$ 0 , $[\theta]_{200}$ +30000!
13	238 nm (ε=29000)	$[\theta]_{295}$ 0 , $[\theta]_{246}$ -149000 (neg.max.) , $[\theta]_{231}$ 0 ,
	244 nm (sh. ε=28500)	$[\theta]_{223}$ +45000 (pos.max.) , $[\theta]_{214}$ +25000 (pos.min.) , $[\theta]_{200}$ +83000!
14	239 nm (ε=28000)	$[\theta]_{295}$ 0 , $[\theta]_{247}$ -114000 (neg.max.) , $[\theta]_{232}$ 0 ,
	247 nm (sh. ε=27500)	$[\theta]_{224}$ +51000 (pos.max.) , $[\theta]_{211}$ +23000 (pos.min.) , $[\theta]_{200}$ +61000!

! end absorption

Table II. ^{13}C NMR Data for 5, 6, 9, 11, 13, and 14[a]

Carbon	5	6	9	11	13	14
1	173.1(s)	173.2(s)	172.9(s)	63.2(t)	62.8(t)	63.0(t)
2	29.2(t)[b]	29.5(t)[b]	29.3(t)[b]	28.0(t)[b]	28.6(t)	28.7(t)
3	29.8(t)[b]	29.8(t)[b]	29.7(t)[b]	34.7(t)	31.1(t)	31.6(t)
4	73.4(d)	73.3(d)	73.2(d)	72.2(d)	74.9(d)	70.6(d)
5	133.1(d)	133.2(d)	133.5(d)[c]	139.4(d)	132.4(d)	129.8(d)
6	126.6(d)	125.8(d)	127.4(d)	124.1(d)	124.0(d)[b]	126.3(d)
7	128.3(d)	128.4(d)	128.1(d)	128.3(d)	128.0(d)	119.7(d)
8	148.9(s)	144.2(s)	144.5(s)	144.5(s)	151.6(s)	152.9(s)
9	75.5(d)	76.2(d)	78.7(d)	75.1(d)	75.5(d)	75.7(d)
10	32.0(t)	29.8(t)[b]	30.0(t)	32.3(t)	32.6(t)	32.6(t)
11	37.1(t)	37.8(t)	38.6(t)	37.5(t)	39.1(t)	39.0(t)
12	88.0(s)	87.6(s)	87.3(s)	89.4(s)	79.3(s)	79.4(s)
13	32.6(t)	33.7(t)	34.5(t)	32.9(t)	36.0(t)	36.2(t)
14	123.1(d)	123.0(d)	123.3(d)	123.6(d)	124.2(d)[b]	124.1(d)
15	134.2(d)	134.5(d)	133.8(d)[c]	134.4(d)	133.5(d)	133.8(d)
16	27.5(t)	27.6(t)	27.6(t)	27.7(t)[b]	27.5(t)	27.6(t)
17	29.4(t)[b]	29.3(t)[b]	29.3(t)[b]	29.3(t)	29.3(t)	29.3(t)
18	31.5(t)	31.6(t)	31.5(t)	31.6(t)	31.6(t)	31.6(t)
19	22.5(t)	22.6(t)	22.5(t)	22.6(t)	22.6(t)	22.6(t)
20	14.0(q)	14.1(q)	14.0(q)	14.1(q)	14.1(q)	14.1(q)
COO$\underline{CH}_3$	51.7(q)	51.7(q)	51.6(q)			
$CH_3\overset{\|\|}{\underset{O}{C}}$- x 2	170.8(s)	170.0(s)	169.7(s)			
	170.0(s)	169.5(s)	169.4(s)			
	21.6(q)	21.7(q)	21.4(q)			
	21.1(q)	21.2(q)	21.0(q)			

a) Abbreviations given in parentheses denote the signal patterns observed in off-resonance experiments: d=doublet, q=quartet, s=singlet, t=triplet.

b), c) The assignments for these signals within the same vertical column may be interchanged.

trisilyl ether (10), $C_{38}H_{76}O_4Si_3$ and a disilyl ether (12), $C_{32}H_{62}O_4Si_2$. Subsequent esterification of 10 with *p*-nitrobenzoyl chloride and pyridine in the presence of AgCN[6] furnished the *p*-nitrobenzoate (11), $C_{45}H_{79}NO_7Si_3$, IR (CCl_4): 1718 cm^{-1}. The ^1H NMR spectrum (200 MHz, $CDCl_3$) of 11 showed signals due to its skeletal protons[7] : δ 3.53 (2H, br s, 1-H_2), 4.16 (1H, m, 4-H), 5.69 (1H, dd, J=15, 5 Hz, 5-H), 6.70 (1H, dd, J=15, 12, 6-H), 6.17 (1H, dd, J=12, 2, 7-H), 4.38 (1H, br t, J=8, 9-H), 3.11, 2.73 (2H, AB in ABX, J_{AB}=14, J_{AX}=8, J_{BX}=7, 13-H_2), 5.35 (1H, m, 14-H), 5.55 (1H, m, 15-H), together with signals due to three *t*-butyldimethylsilyl (TBDMS) residues and a *p*-nitrobenzoyl group. In addition, among the ^{13}C NMR signals assigned as given in Table II, a signal due to C-12 was observed at δc 89.4; thus *p*-nitrobenzoylation of 12-OH in **11** has been proved. The CD spectrum of **11** showed a positive first Cotton effect (Table I); thus the absolute C-12 configuration in **10** has been corroborated as R (*cf.* Fig. 1).[7)]

On the other hand, benzoylation of **12** furnished a monobenzoate (**13**), $C_{39}H_{66}O_5Si_2$, IR (CCl_4): 3590 (OH), 1712 (CO), ^1H NMR[8)]: δ 3.65 (2H, t, J=6 Hz, 1-H_2), 5.60 (1H, dt, J=7, 6, 4-H), 5.74 (1H, dd, J=15, 7, 5-H), 7.07 (1H, dd, J=15, 11.5, 6-H), 6.11 (1H, d, J=11.5, 7-H), 4.29 (1H, br t, J=7, 9-H), 2.58, 2.40 (2H, AB in ABX, J_{AB}=14, J_{AX}=8, J_{BX}=7, 13-H_2), 5.30 (1H, m, 14-H), 5.50 (1H, m, 15-H), together with signals due to two TBDMS residues and one benzoyl group. The signal at δ 5.60 showed that the 4-OH group in **12** was benzoylated to give **13**. We then applied to **13** the exciton chirality rule, which was recently extended to acyclic allylic benzoates by Nakanishi et al.[9)] Since the $J_{4,5}$ value of **13** was 7 Hz (in CD_3OD) and the CD spectrum of **13** (in MeOH) showed a negative first Cotton effect, **13** has been considered to take a conformation in MeOH as depicted in Fig. 1. Thus, the C-4 absolute configuration has been assigned R. The assignment has been further supported by a similar CD curve observed for **14**, $C_{39}H_{66}O_5Si_2$, which was prepared from claviridenone-d (**4**) through the same procedure as that for **13** from **3**.

Based on the above-mentioned evidence, the absolute stereostructures of claviridenone-a (**1**), -b (**2**), -c (**3**), and -d (**4**) have been determined.

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4) The structures of compounds (**5** - **14**) have been substantiated by the ^{13}C NMR analysis in detail as partly shown in Table II.
5) The molecular compositions of compounds with the chemical formulae were determined by high resolution mass spectrometry.
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7) The 12-benzoate of **10** showed a rather complicated CD spectrum, which was presumably due to a CD Cotton effect of opposite sign of the inherent 5,7-diene chirality in this benzoate. The similar tendencies were observed more or less throughout all compounds having the 5,7-diene chromophore, which will be discussed in detail in our full paper.
8) The assignments for skeletal protons have been made on the basis of spin-decoupling experiments in detail.
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(Received March 9, 1983)