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MARINE NATURAL PRODUCTS—XV

POLYHALOGENATED CYCLIC MONOTERPENES FROM THE RED ALGA *PLOCAMIUM CARTILAGINEUM* OF ANTARCTICA

DONALD B. STIERLE and JAMES J. SIMS*
Departments of Plant Pathology and Chemistry, University of California, Riverside, CA 92521, U.S.A.

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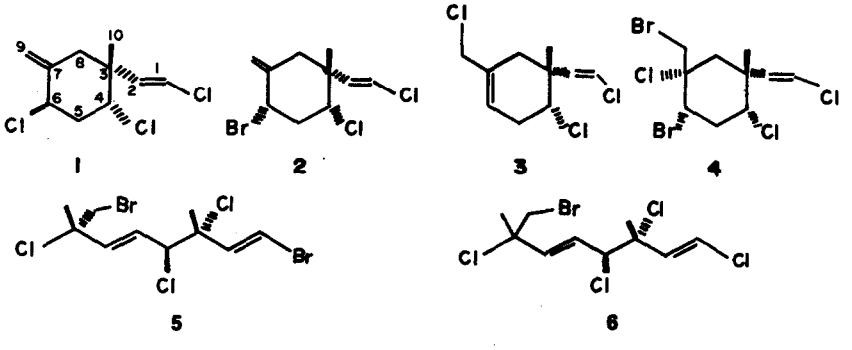
Abstract—Examination of the red alga *Plocamium cartilagineum* (L.) Dixon collected along the Antarctic Peninsula yielded several new cyclic halogenated monoterpenes. The structures of a 2,4-dichloro-*trans*-1-chlorovinyl-1-methyl-5-methylene-cyclohexane, a 2-chloro-4-bromo-*trans*-1-chlorovinyl-1-methyl-5-methylene-cyclohexane, a 2-chloro-*trans*-1-chlorovinyl-1-methyl-5-chloromethyl-4-cyclohexene, and a 2,5-dichloro-4-bromo-*trans*-1-chlorovinyl-1-methyl-5-bromomethyl-cyclohexane are described. The structures were determined by spectroscopic methods and chemically related to the halogenated monoterpene violacene.

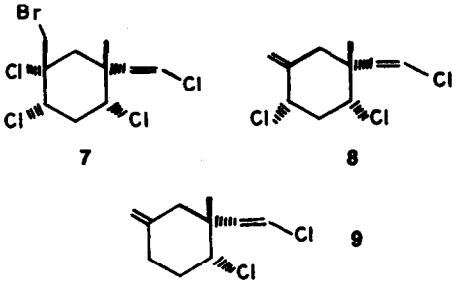
Red algae have recently been shown to contain many halogenated terpenes.[1,2] Species of the genus *Plocamium* have been an especially rich source of acyclic and cyclic halogenated monoterpenes.[1,2] In their investigation of the macroscopic algae of Antarctica, De Laca *et al.*[3] collected and sent varying amounts of *Plocamium* species to us for chemical investigation. In this paper we wish to describe a family of polyhalogenated cyclic compounds isolated from *Plocamium cartilagineum* (L.) Dixon.

Plocamium cartilagineum[4] was collected subtidally by divers off the north shore of Janus Island along the Antarctic Peninsula. The alga, which was received frozen, was air-dried, ground in a Wiley Mill and extracted with hexane in a Soxhlet apparatus. Concentration of the hexane gave a dark green oil. The extract was spotted onto a tlc plate, developed with chloroform, sprayed with spores of the fungus *Cladosporium cucumerinum* and allowed to incubate.[5] Strong antifungal activity was observed at several spots on the plate. Open column chromatography of the extract on silica gel using hexane with increasing amounts of diethyl ether as the elutant followed by repeated high pressure liquid chromatography (hplc) on silica gel gave pure 1, 2 and 4, hplc of one of the fractions on alumina yielded 3 and the two acyclic monoterpenes 5 and 6.[6]

High resolution mass spectrometry established the molecular formula of 1 as $C_{10}H_{13}Cl_3$. This formula requires three sites of unsaturation. The ^{13}C spectrum of 1 contained four resonances assigned to olefinic C atoms, thus requiring the compound to contain one ring. The structure of the compound was mainly deduced by combination of evidence from CMR and PMR spectra. A pair of doublet resonances (120.3 and 134.1 ppm) in the off-resonance CMR indicated a disubstituted double bond.[7] The hydrogens on this double bond gave rise to a pair of doublets at 6.00 and 6.10 δ in the 220 MHz PMR spectrum. The double bond was assigned the *trans* configuration because of the 13.1 Hz coupling constant. The proton and carbon chemical shifts required that one of the chlorines be attached to this double bond. The second double bond was evidenced by CMR absorptions at 113.6 (triplet) and 140.9 (singlet) ppm and was assigned as an exocyclic olefin. In the PMR spectrum, two broad singlets at 4.93 and 5.18 δ were assigned to the exocyclic methylene protons. Two methine carbons gave absorption at 63.2 and 61.5 (doublets); the chemical shifts indicating that a chlorine was attached to each.[8] In the PMR, a broadened triplet at 4.72 δ (J = 3.2 Hz) and a doublet of doublets at 4.33 δ (J = 11.1 and 3.6 Hz) were assigned to the methine protons. Each of the methine protons was coupled to the complex methylene multiplet absorbing from 2.18 to 2.43 δ indicating a –CHCl–CH_2–CHCl grouping. Two methylene carbons were evidenced by absorptions at 41.5 and 41.1 ppm (triplets). One was assigned as the methylene of the –CHCl–CH_2–CHCl– grouping and the other as an isolated methylene. The proton absorption of the isolated methylene was an AB pattern at 2.36 and 2.64 δ with a geminal coupling constant of 14.5 Hz. A quaternary carbon was recognized by a singlet absorption in the CMR at 43.5 ppm. The remaining carbon was a quaternary Me which gave rise to CMR absorption at 26.6 ppm (quartet) and a singlet resonance at 1.25 δ in the PMR spectrum.



The spectral analysis above plus comparison with spectral data reported for other compounds isolated from *Plocamium* species support structure 1. We confirmed the structure including full stereochemistry by comparison to derivatives of violacene 7. Violacene was isolated as the major halogenated constituent of *Plocamium violaceum* by Mynders *et al.*[9] We reisolated it and repeated the chromous sulfate[10] reduction previously described to yield both dibromochloroviolacene,[9] 8, and the further reduced compound 9.[11] The 220 MHz PMR spectra of 1 and 8 were similar but differed significantly in the multiplicity and chemical shifts of the absorptions assigned to the C_6 protons (Table 1, Hf). In the spectrum of 1, this proton appeared as a broadened triplet at 4.72 δ and in that of 8 as a broadened doublet of doublets at 4.26 δ. The most likely explanation was that 1 and 8 were epimers at C_6. Confirmation was obtained by treatment of 1 with chromous sulfate yielding 9 identical in all respects to 9 produced by reduction of violacene.

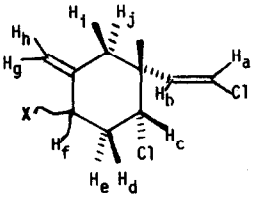


7 8 9

The molecular formula $C_{10}H_{13}BrCl_2$ for compound 2 was established by high resolution mass spectrometry. Comparison of the 220 MHz PMR spectra (CCl_4) of compound 2 and debromochloroviolacene 8 suggested their structural similarity (Table 1). All of the proton chemical shifts of 2 were very close or identical to those of 8 except for the CH–CH_2–CH moiety. In the PMR spectrum of 2 Hf, which was adjacent and allylically coupled (1 Hz) to the exocyclic methylenes, appeared as a doublet of doublets (J = 12.0 and 4.5 Hz) at 4.37 δ. In the spectrum of 8 Hf also appeared as a doublet of doublets (J = 12.3 and 4.0 Hz) at 4.26 δ. The coupling constants of these protons indicated that each proton was in an axial position. Lack of significant change in chemical shift of any of the other protons on the ring indicated that both compounds had the same relative stereochemistry around C_6. The downfield shift of Hf in 2 was evidence for a substitution of a chlorine by bromine[7] at C_6. Chromous sulfate reduction of 2 gave a compound identical by PMR, IR, MS and optical rotation to 9 obtained from the reduction of violacene. This confirms the relative and absolute stereochemistry assigned to 2.

When compound 2 was allowed to stand at room temperature for a few days, it underwent a quantitative rearrangement to an isomeric compound. The CMR spectrum of the isomer displayed absorption for the usual disubstituted vinyl chloride group and a new trisubstituted double bond at 133.0 (off-resonance singlet) and 124.7 ppm (doublet). In the proton spectrum, the exocyclic methylene proton resonances had disappeared and were replaced by a broad one proton singlet at 5.73

Table 1. Proton chemical shifts of compounds 1, 2 and 8, 220 MHz (CCl_4)



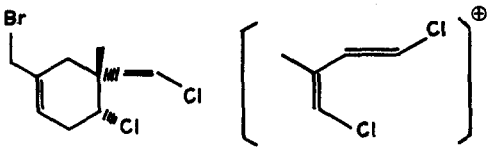
	X	H_a	H_b	H_c	H_d and H_e	H_f	H_g	H_h	H_i or H_j	CH_3
1	β-Cl	6.10(d)	6.00(d)	4.33(dd)	2.43-2.18(m)	4.72(bt)	5.18(bs)	4.93(bs)	2.64(d) 2.36(d)	1.25(s)
		J_{ab}=13.3Hz		J_{cd}=11.1Hz		J_{ef}=3.2Hz			J_{ij}=14.5Hz	
				J_{ce}=4.5Hz						
2	α-Br	6.06(d)	5.95(d)	3.74(dd)	2.70-2.62(m)	4.37(dd)	5.43(bs)	5.05(bs)	2.30(d) 2.17(d)	1.23(s)
		J_{ab}=13.5Hz		J_{cd}=12.3Hz		J_{df}=12.0Hz			J_{ij}=13.5Hz	
				J_{ce}=4.5Hz		J_{ef}=4.5Hz				
8	α-Cl	6.06(d)	5.96(d)	3.78(dd)	2.63-2.50(m)	4.26(dd)	5.43(bs)	5.01(bs)	2.23(d) 2.12(d)	1.26(s)
		J_{ab}=13.5Hz		J_{cd}=12.5Hz		J_{df}=12.3Hz			J_{ij}=13.0Hz	
				J_{ce}=4.5Hz		J_{ef}=4.0Hz				

Table 2. Carbon chemical shifts of compounds 1, 2, 8 and 9, 22.6 MHz ($CDCl_3$)

	X	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
1	β-Cl	120.3(d)	134.1(d)	43.5(s)	63.2(d)	41.5(t)*	61.5(d)	142.3(s)	41.1(t)*	115.3(t)	26.5(q)
2	α-Br	120.6	133.5	43.3	65.5	44.1*	49.3	140.7	45.2*	116.1	26.2
8	α-Cl	120.7(d)	133.3(d)	43.4(s)	65.1(d)	43.4(t)*	58.2(d)	140.9(s)	45.5(t)*	113.6(t)	26.2(q)
9	H	119.1	136.3	43.4	67.9	32.7*	32.9*	143.2	44.6	111.4	26.1

* assignments may be reversed

δ. Absorption for the methine proton adjacent to the exocyclic methylene of 2 had also disappeared and a two proton singlet appeared at 3.87 δ. The carbon spectrum of the isomer displayed a triplet at 37.2 ppm for this carbon. A reasonable interpretation of this data is an allylic rearrangement of 2 to give the product 10. Additional support for structure 10 was found in the mass spectrum. Compound 10 did not display a parent ion but did show loss of chlorine and bromine. The base peaks appeared at *m/e* 136/138/140 (Cl_2 pattern) which was assigned to the reverse Diels–Alder fragment 11. This fragmentation has been well documented in cyclohexenes.[12]

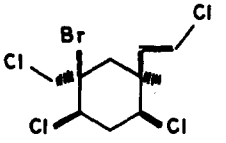


10 11

It is interesting to note, that despite this facil rearrangement, 10 was not isolated as a natural product. However, a compound similar in structure to 10 was isolated from this alga. Compound 3 was found to be isomeric with 1 by high resolution mass spectrometry. The 220 MHz proton spectrum (CCl_4) (Table 3) of 3 was almost identical to that of 10. The CMR spectra (Table 4) of both 3 and 10 were also very similar except for a downfield shift (37.2–48.9 ppm) of the halomethylene carbon. This shift is indicative for replacement of a bromine by a chlorine.[7] The base peaks in the mass spectrum also (as in 10) appeared at *m/e* 136/138/140 (Cl_2 pattern) and was assigned to 11, the reverse Diels–Alder fragment. Chromous sulfate reduction of 3 gave only one product, that was identical in every way to 9, the reduction product of violacene. It was at first surprising to obtain the same reduction product from 1 and 3. However, based on Castro's work on the chromous ion reduction, both compounds should reduce through a common intermediate.[10] Compound 3 must then have the relative and absolute stereochemistry shown.

Compounds 1, 2 and 3, which were the major metabolites isolated from this alga were all debromochloro derivatives of violacene. Isolated in much smaller amounts was 4 a derivative of violacene. The molecular formula of $C_{10}H_{13}Br_2Cl_3$ was established for 4 by high resolution mass spectrometry.

The 200 MHz proton spectrum (CCl_4) of 4 suggested its structural similarity to violacene 7 (Table 5). Compound 3 contained 2 bromines and 3 chlorines while violacene contained 1 bromine and 4 chlorines. The ^{13}C spectra of 4 and 7 indicated that the extra bromine in 4 was located at one of the methine carbons (Table 6). Reduction of 4 with two equivalents of chromous sulfate gave a compound that was identical to 9 in every way, the reduction product of violacene. This established the extra bromine in 4 to be at C_6. From the coupling constants displayed (J = 12.3, 4.0 Hz) by Hf, it was axial. This established the relative and absolute stereochemistry at C_3, C_4 and C_6. From the similarities in proton and carbon spectra it was felt that the stereochemistry at C_7 was also identical to that of violacene.



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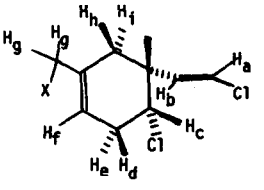
Full assignment of the ^{13}C NMR spectrum for compound 1 could be accomplished by consideration of the chemical shifts and off-resonance multiplicities.[7,13,14] The carbons of the chlorovinyl group were related to those in violacene which were assigned by the true coupling constant.[8] In an off-resonance experiment, the residual coupling constant, J^r, is proportional to the chemical shift difference of the proton absorption and the decou-

Table 3. Proton chemical shifts of 3 and 10, 220 MHz (CCl_4)

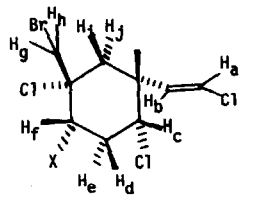


	X	H_a	H_b	H_c	H_d and H_e	H_f	H_g	H_h or H_i	CH_3
3	Cl	6.05(d) J_{ab}=13.1Hz	5.97(d)	3.87(dd) J_{cd}=9.0Hz J_{ce}=4.5Hz	2.50–2.28(m)	5.68(bs)	3.94(s)	2.60(d) 2.14(d) J_{hi}=18.0Hz	1.24(s)
10	Br	6.08(d) J_{ab}=13.5Hz	5.98(d)	3.87(dd) J_{cd}=8.9Hz J_{ce}=4.5Hz	2.51–2.41(m)	5.73(bs)	3.87(s)	2.60(d) 2.22(d) J_{hi}=17.9Hz	1.24(s)

Table 4. Carbon chemical shifts of 3 and 10, 22.6 MHz ($CDCl_3$)

	X	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	CH_3
3	CL	119.1(d)	135.3(d)	40.7(s)	64.2(d)	33.7(t)	124.4(d)	132.4(s)	36.7(t)	48.9(t)	25.6(q)
10	Br	119.1(d)	135.3(d)	40.7(s)	64.1(d)	33.9(t)	124.7(d)	133.0(s)	37.2(t)	37.2(t)	25.6(q)

Table 5. Proton chemical shifts of 4 and 7, 220 MHz (CCl_4)



	X	H_a	H_b	H_c	H_d	H_e	H_f	H_g	H_h	H_i or H_j	CH_3
4	Br	6.50(d) J_{ab}=13.6Hz	6.02(d)	3.75(dd) J_{cd}=13.3Hz J_{ce}=3.9Hz	2.56(ddd) J_{de}=13.6Hz	2.79(ddd)	4.44(dd) J_{df}=12.3Hz J_{ef}=4.0Hz	3.95(d) J_{gh}=10.6Hz	3.51(d)	2.25(d) 2.40(d) J_{ij}=15.2Hz	1.29(s)
7	Cl	6.44(d) J_{ab}=13.5Hz	6.02(d)	3.64(dd) J_{cd}=12.0Hz J_{ce}=4.0Hz	2.44(ddd) J_{de}=14.0Hz	2.64(ddd)	4.29(dd) J_{df}=12.0Hz J_{ef}=4.0Hz	3.95(d) J_{gh}=10.5Hz	3.48(d)	2.16(d) 2.32(d) J_{ij}=15.0Hz	1.29(s)

Table 6. Carbon chemical shifts of 4 and 7, 22.6 MHz ($CDCl_3$)

	X	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	CH_3
4	Br	119.2	135.4	42.1	64.8	40.4	51.2	70.9	48.6	39.2	27.5
7	Cl	119.5(d)	135.4(d)	42.0(s)	64.1(d)*	38.3(t)	59.0(d)*	71.3(s)	48.8(t)	38.8(t)	27.4(q)

*assignments reversed from original, assigned by J^r

pler frequency offset.[15] If two proton resonances differ in chemical shift, the carbons to which they are attached can be assigned by examination of J^r. Carbons 4 and 6 in structure 1 could be assigned by their J^r's.

The carbon spectra of compounds 2, 8 and 9 were assigned by comparison to the chemical shifts in 1. Change from an axial chlorine, as in compound 1, to an equatorial chlorine, as in 8 relieves some 1,3 interactions at C_4 and C_8 shifting these carbon absorptions to lower field.[16] The conformation(s) of the ring in compounds 2 and 8 are very similar as can be seen from the proton coupling constants. Substitution of a bromine for a chlorine should then only change the chemical shift of the carbon directly bonded to the halogen. This is indeed the case.

^{13}C assignments for compounds 3 and 10 could also be made using the chemical shifts and multiplicities. Of the two methylene triplets observed in the off-resonance spectrum, the lower field resonance was assigned to C_8 because it is β to a quaternary carbon.[17]

While this work was in progress, the original structure, 12, proposed for violacene[9] was revised[18] to 7 based on an X-ray diffraction study. We had come to the same conclusion based on the ^{13}C NMR spectra accumulated in this laboratory. In particular, the resonance at 38.8 ppm in violacene has to be assigned to a bromomethylene rather than a chloromethylene.

Assignments for the CMR of violacene, 7 have previously been made by Mynderse[11] and Crews.[8] Our study of violacene included an off-resonance experiment which revealed the J^r's of each carbon. With irradiation at −4 in the proton region, the carbon resonance at 59.0 ppm displayed a larger J^r than the resonance at 64.1 ppm. Since the proton attached at C_6 resonates furthest downfield in the PMR spectrum, this has to be assigned to the upfield carbon resonance (59.0 ppm). This is a reversal from the original assignments. Assignments for compound 4 were based on the chemical shifts found in violacene.

Many of the halogen containing compounds isolated from marine algae exhibit antibiotic activity.[1,19] Fenical has proposed that these compounds are produced to discourage invertebrate predators and as a defense against parasitic microflora.[1] Compounds 1–4 were tested individually against the fungus *Cladosporium cucumerinum* on a tlc plate[5] and were found to have moderate activity.

EXPERIMENTAL

Optical rotations were determined on a Jasco ORD-CD spectrometer with a 1-cm cell (1 ml). IR spectra were taken on a Perkin–Elmer Model 137 spectrophotometer. PMR spectra were recorded on a Varian HR-220 spectrometer. Carbon NMR spectra were recorded on a Bruker WH-90 multinuclear spectrometer. The frequency offset in the off-resonance experiments was at −4 δ with a power of 3340 Hz. Low resolution mass spectra were done on a Finnigan 1015 S/L spectrometer. High resolution mass spectra were recorded by Dr. Kai Fang, Department of Chemistry, UCLA. High pressure liquid chromatography was performed on a Waters Associates instrument with the M-6000 pump.

Collection and extraction. Plocamium cartilagineum was collected subtidally by divers off the north shore of Janus Island, Antarctic Peninsula. The alga was received frozen but was air-dried when received. The alga (350 g) was ground in a Wiley mill and extracted with hexane in a Soxhlet apparatus. The solvent was removed under reduced pressure to give 3.9 g of a dark green oil.

Silica gel chromatography. The crude extract (3.9 g) was applied to a 3 × 50 cm silica gel column (Grace, grade 62) and the monpolar oil eluted using hexane with increasing amounts of diethyl ether. Fraction 1 contained non-halogenated hydrocarbons (80 mg), fractions 2 and 3 contained mostly 1 (150 mg), fraction 4 contained mostly 2 and small amounts of 3 (200 mg), fraction 5 contained mostly 3 (110 mg) and fractions 6 and 7 contained a mixture of 4, 5 and 6 (420 mg).

High pressure liquid chromatography. Column chromatography fractions were further purified by high pressure liquid chromatography. Compounds 1, 2 and 3 were purified on a 1/2 in. × 6 ft column packed with Bio-Sil A (20–44 μ) using hexane–EtOAc as the solvent. Compounds 4, 5 and 6 were purified on a 1/4 in. × 2 ft

column packed with Woelm alumina (18 μ) using hexane–EtOAc as the solvent.

Compound 1 $[\alpha]_D = -63.3°$ ($c = 0.98$, $CHCl_3$); IR (μ) 3.22, 2.27, 6.02, 6.92, 8.10, 10.84, 12.25; PMR (220 MHz, CCl_4) δ 1.25 (3H, s), 2.43–2.18 (2H, m), 2.36 (1H, d, J = 14.5 Hz), 2.64 (1H, d, J = 14.5 Hz), 4.33 (1H, dd, j = 11.1, 3.6 Hz), 4.72 (1H, bt, J = 3.2 Hz), 4.93 (1H, bs), 5.18 (1H, bs), 6.00 (1H, d, J = 13.1 Hz), 6.10 (1H, d, J = 13.1 Hz); CMR ($CDCl_3$) ppm 26.5 (q), 41.1 (t), 41.5 (t), 43.5 (s), 61.5 (d, J^r = 43.0 Hz), 63.2 (d, J^r = 38.5 Hz), 115.3 (t), 120.3 (d), 134.1 (d), 142.3 (s); Mass spectrum *m/e* 238, 240, 242 (M^+), 203, 205, 207 (M^+–Cl), 167, 169 (M^+–HCl_2) (BP), 105 ($C_8H_9^+$), 91 ($C_7H_7^+$). High resolution mass measurement. Calc. for $C_{10}H_{13}{}^{35}Cl_2{}^{37}Cl$: 240.0053. Obs: 240.0060 ± 001.

Compound 2 $[\alpha]_D = +31.3°$ ($c = 0.86$, $CHCl_3$); IR (μ) 3.25, 3.36, 6.01, 6.89, 10.55; PMR (220 MHz, CCl_4) δ 1.23 (3H, s), 2.17 (1H, d, J = 13.5 Hz), 2.30 (1H, d, J = 13.5 Hz), 2.70–2.62 (2H, m), 3.74 (1H, dd, J = 12.3, 4.5 Hz), 4.37 (1H, bdd, J = 12.0, 4.5 Hz), 5.05 (1H, bs), 5.43 (1H, bs), 5.95 (1H, d, J = 13.5 Hz), 6.06 (1H, d, J = 13.5 Hz); CMR ($CDCl_3$) ppm 26.2, 43.3, 44.1, 45.2, 49.3, 65.5, 116.1, 120.6, 133.5, 140.7; Mass spectrum *m/e* 282, 284, 286 (M^+), 247, 249, 251 (M^+ Cl), 203, 205, 207 (M^+–Br), 131 ($C_{10}H_{11}^+$)(BP), 105 ($C_8H_9^+$). High resolution mass measurement. Calc. for $C_{10}H_{13}{}^{79}Br^{35}Cl_2$: 281.9578. Obs: 281.9583 ± 001.

Compound 3 $[\alpha]_D = -110°$ ($c = 0.91$, $CHCl_3$); IR (μ) 3.40, 6.18, 7.93, 10.57, 13.16; PMR (220 MHz, CCl_4) δ 1.24 (3H, s), 2.14 (1H, d, J = 18.0 Hz), 2.50–2.28 (2H, m), 2.60 (1H, d, J = 18.0 Hz), 3.87 (1H, dd, J = 9.0, 4.5 Hz), 3.94 (2H, s), 5.68 (1H, bs), 5.97 (1H, d, J = 13.5 Hz), 6.05 (1H, d, J = 13.5 Hz); CMR ($CDCl_3$) ppm 25.6 (q), 33.7 (t), 36.7 (t), 40.7 (s), 48.9 (t), 64.2 (d), 119.1 (d), 124.4 (d), 132.4 (s), 135.3 (d); Mass spectrum *m/e* 238, 240, 242 (M^+), 203, 205, 207 (M^+–Cl), 136, 138, 140 ($C_5H_6Cl_2^+$) (BP), 105 ($C_8H_9^+$), 91 ($C_7H_7^+$). High resolution mass measurement. Calc. for $C_{10}H_{13}{}^{35}Cl_2{}^{37}Cl$: 240.0053. Obs: 240.0060 ± 001.

Compound 4 $[\alpha]_D = -67.8°$ ($c = 1.33$, $CHCl_3$); IR (μ) 3.35, 7.00, 10.70, 12.03, 13.16; PMR (220 MHz, CCl_4) δ 1.29 (3H, s), 2.25 (1H, d, J = 15.2 Hz), 2.40 (1H, d, J = 15.2 Hz), 2.56 (1H, ddd, J = 13.6, 4.0, 3.9 Hz), 2.79 (1H, ddd, J = 13.6, 12.3, 4.0 Hz), 3.51 (1H, d, J = 10.6 Hz), 3.65 (1H, dd, J = 13.3, 3.9 Hz), 3.95 (1H, d, J = 10.6 Hz), 4.44 (1H, dd, J = 12.3, 4.0 Hz), 6.02 (1H, d, J = 13.6 Hz), 6.50 (1H, d, J = 13.6 Hz); CMR $CDCl_3$) ppm 27.5, 39.2, 40.4, 42.1, 48.6, 51.2, 64.6, 70.9, 119.2, 135.4; Mass spectrum *m/e* 396, 398, 400, 402 (M^+), 361, 363, 365, 367 (M^+–Cl), 317, 319, 321, 323 (M^+–Br), 91 ($C_7H_7^+$) (BP). High resolution mass measurement. Calc. for $C_{10}H_{13}{}^{79}Br_2{}^{35}Cl_3$: 395.8451. Obs: 395.8460 ± 001.

Rearrangement of 2 *to* 10. IR (μ) 3.40, 6.97, 8.25, 10.59, 13.90; PMR (220 MHz, CCl_4) δ 1.24 (3H, s), 2.22 (1H, d, J = 17.9 Hz), 2.51–2.41 (2H, m), 2.60 (1H, d, J = 17.9 Hz), 3.87 (2H, s), 3.87 (1H, dd, J = 8.9, 4.5 Hz), 5.73 (1H, bs), 5.98 (1H, d, J = 13.5 Hz), 6.08 (1H, d, J = 13.5 Hz); CMR ($CDCl_3$) ppm 25.6 (q), 33.9 (t), 37.2 (2C, m), 40.7 (s), 64.1 (d), 119.1 (d), 124.7 (d), 133.0 (s), 135.3 (d); Mass spectrum *m/e* 247, 249, 251 (M^+–Cl), 203, 205, 207 (M^+–Br), 136, 138, 140 ($C_5H_6Cl_2^+$), 131 ($C_{10}H_{11}^+$), 79 ($C_6H_7^+$).

Reduction of violacene (7) *with chromous sulfate.* Aqueous $CrSO_4$ was prepared by a modified method of Castro *et al.* using Zn dust that had been activated by washing with dil. HCl.[10] In a flask fitted with a septum stopple and N_2 inlet and outlet was placed 20 ml of freshly distilled DMF. N_2 was run over the DMF for 10 min and then 4 ml of fresh $CrSO_4$ soln (1.10 mmoles) was added by means of a syringe. Violacene 7 (200 mg; 0.568 mmoles) was dissolved in 3 ml of DMF and added slowly to the $CrSO_4$ soln, the soln turned from a deep blue to a deep green. After 30 min, 30 ml of water was added and the soln extracted 2 × 20 ml of diethyl ether. The ether layers were washed 2 × 10 ml of water and dried over $MgSO_4$. The $MgSO_4$ was filtered off and the ether removed to give 143 mg of a clear oil. Hplc of the oil gave 60 mg of 8, 55 mg of 9, and 20 mg of violacene.

Compound 8 $[\alpha]_D = +33.0°$ ($c = 0.77$, $CHCl_3$); IR (μ) 3.35, 6.88, 9.94, 10.90, 12.15, 13.46; PMR (220 MHz), CCl_4) δ 1.26 (3H, s), 2.12 (1H, d, J = 13.0 Hz), 2.23 (1H, d, J = 13.0 Hz), 2.50–2.63 (2H, m), 3.78 (1H, dd, J = 12.5, 4.5 Hz), 4.26 (1H, bdd, J = 12.3, 4.0 Hz), 5.01 (1H, bs), 5.43 (1H, bs), 5.96 (1H, d, J = 13.5 Hz), 6.06 (1H, d, J = 13.5 Hz); CMR ($CDCl_3$) ppm 26.2 (q), 43.4 (2C), 45.5 (t), 58.2 (d), 65.1 (d), 113.6 (t), 120.7 (d), 133.3 (d), 140.9 (s); Mass spectrum *m/e* 238, 240, 242 (M^+), 203, 205, 207 (M^+–Cl), 167, 169 (M^+–HCl_2) (BP), 131 ($C_{10}H_{11}^+$), 91 ($C_7H_7^+$).

Compound 9 $[\alpha]_D = -25.1°$ ($c = 0.55$, $CHCl_3$); IR (μ) 3.40, 6.00, 6.86, 10.55, 11.09, 12.03; PMR (220 MHz, CCl_4) δ 1.19 (3H, s), 1.79–2.20 (4H, m), 2.37–2.52 (2H, m), 3.82 (1H, dd, J = 9.9, 3.6 Hz), 4.68 (1H, bs), 4.79 (1H, bs), 5.99 (2H, s); CMR ($CDCl_3$) ppm 26.1, 32.7, 32.9, 43.4, 44.6, 67.9, 111.4, 119.1, 136.3, 143.2; Mass spectrum *m/e* 204, 206, 208 (M^+), 169, 171 (M^+–Cl) (BP), 105 ($C_8H_9^+$).

Reduction of 1 *with chromous sulfate.* The procedure as described above was repeated using 1, 30 mg (0.13 mmoles) and 1 ml (0.27 mmoles) of $CrSO_4$ solution. Hplc of the oil gave 10 mg of a compound that had PMR, IR and MS identical to 9. $[\alpha]_D = -23°$.

Reduction of 2 *with chromous sulfate.* The procedure as described above was repeated using 2, 30 mg (0.12 mmoles) and 1 ml (0.27 mmoles) of $CrSO_4$ solution. Hplc of the oil gave 17 mg of a compound that had PMR, IR and MS identical to 9. $[\alpha]_D = -22°$.

Reduction of 3 *with chromous sulfate.* The procedure as described above was repeated using 3, 30 mg (0.13 mmoles) and 1 ml (0.27 mmoles) of $CrSO_4$ solution. Hplc of the oil gave 10 mg of a compound that had PMR, IR and MS identical to 9. $[\alpha]_D = -24°$.

Reduction of 4 *with chromous sulfate.* The procedure as described above was repeated using 4, 25 mg (0.07 mmoles) and 1.1 ml (0.28 mmoles) of $CrSO_4$ solution. Hplc of the oil gave 9 mg of a compound that had PMR, IR and MS identical to 9. $[\alpha]_D = -23°$.

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