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Haydelba T. D'Armas, Baldwin S. Mootoo, and William F. Reynolds

Department of Chemistry, University of the West Indies, St. Augustine, Trinidad and Tobago, and Department of Chemistry, University of Toronto, Ontario M5S1A1, Canada



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An Unusual Sesquiterpene Derivative from the Caribbean Gorgonian Pseudopterogorgia rigida

Haydelba T. D'Armas, Baldwin S. Mootoo, *, and William F. Reynolds

Department of Chemistry, University of the West Indies, St. Augustine, Trinidad and Tobago, and Department of Chemistry, University of Toronto, Ontario M5S1A1, Canada

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A new sesquiterpene derivative named mochiquinone (1) was isolated from the Caribbean gorgonian coral Pseudopterogorgia rigida collected off northeastern Venezuela, along with the known compounds, a-curcumene, (-)-curcuphenol, (-)-curcuquinone, and (-)-curcuhydroquinone. The structure of the new compound was determined by spectroscopic analysis of its acetylated derivative and comparison with known compounds.

Earlier investigations of the gorgonian octocoral Pseudopterogorgia rigida Bielshowsky (order Gorgonacea, subclass Octocorallia, phylum Coelenterata), have yielded several bisabolane derivatives. 1-8 As part of our continuing studies on Caribbean gorgonian corals, we have examined the EtOAc extract of this organism collected at Mochima Bay, Sucre, Venezuela. The MeOH-soluble fraction of the organism was further extracted with EtOAc. Si gel column chromatography followed by Si gel preparative TLC of this EtOAc extract of P. rigida afforded an unusual perezone (3) 4,5 derivative, for which we propose the name mochiquinone (1), as well as four sesquiterpenoids previously reported: 2,8 (-)-curcuquinone, (-)-curcuphenol, (-)-curcuhydroquinone, and the corresponding aromatic analogue α -curcumene. (—)-Curcuhydroquinone was fully characterized as its diacetate. These known compounds were characterized by comparison of their spectral data with those reported earlier for these sesquiterpenes. 2,3,6,7

1
$$R^1 = OH, R^2 = {}^{16}CH_2OH$$

2
$$R^1 = OAc, R^2 = {}^{16}CH_2OAc$$

$$3 R^1 = OH_1 R^2 = H$$

Mochiquinone (1) was isolated as a yellow oil. The IR spectrum showed a hydroxy absorption (3450 cm^{-1}) as well as the presence of a p-quinone system (1650, 1630 cm⁻¹). The ¹H NMR spectrum displayed a broad doublet at δ 4.55. which was consistent with an oxymethylene group attached to a quaternary carbon, a broad singlet at δ 2.70 and a singlet at δ 7.06 assignable to aliphatic and aromatic hydroxyl groups. In addition, a triplet at δ 5.02 (vinylic proton), a multiplet at δ 3.06 (methine proton), two methylene signals (δ 1.69 and δ 1.94), two olefinic methyl group resonances at δ 1.55 and δ 1.68, an elefinic methyl at δ 2.13, and a fourth methyl signal as a doublet at δ 1.17 were present and comparable to proton signals of related compounds isolated earlier from P. rigida. 1-3 In addition, the ¹H NMR spectrum of compound 1 appeared to be identical with the natural product perezone isolated from Perezia species,4,8 except that a proton in perezone is replaced by an oxymethylene group in 1. Mochiquinone (1) was isolated as an unstable oil that gradually decomposed on standing. Consequently, this new metabolite was further characterized as its acetylated derivative. Upon acetylation, compound 1 yielded a diacetate (2) as a pale yellow oil. Its molecular formula C₂₀H₂₆O₆ was established by HREIMS (m/z 362.1720; calcd 362.1729) and was consistent with the ¹H and ¹³C NMR spectral data (Table 1). 2D NMR techniques (COSY, HSQC, and HMBC) were used to establish the connectivities. An HSQC experiment showed the direct ¹H-¹³C correlations involving all protonated carbons, while an HMBC experiment allowed the assignment of the nonprotonated carbons. The ¹H NMR spectrum of 2 revealed an olefinic methyl singlet (δ 2.13), two acetyl methyl singlets (δ 2.07 and 2.34), a methine multiplet (δ 3.03), an olefinic triplet (δ 5.03), a methyl doublet (δ 1.2, J = 7.0Hz), and two methyl singlets in the aliphatic region (δ 1.54 and 1.65). In addition, the oxymethylene protons of the o-acetoxymethylene group on the aromatic ring appeared at lower field (δ 5.02) compared with that in compound 1 (δ 4.55) and overlapped with the olefinic signal at δ 5.03.

The ¹³C NMR spectrum of 2 confirmed the presence of four methyl, and one oxymethylene moieties, two methylenes, two methines, five quaternary carbons, two quinone carbonyls (å 180.40 and 185.17), and two acetyl groups. In addition, the COSY spectrum of 2 established the proton relationships in which a methine multiplet (δ 3.03, H-7) in the side chain was coupled to a methyl doublet (δ 1.20, $J = 7.0 \,\mathrm{Hz}, \,\mathrm{H}\text{-}14)$ and to the methylene protons (H-8). The vinylic proton at δ 5.03 (1H, t, J = 7.0 Hz) showed coupling with the protons of the olefinic methyl groups of the prenyl moiety. These cross-peaks confirmed the structure of the side chain. Also, the COSY data indicated that the oxymethylene protons were coupled to the aromatic methyl (H₃-15). The HMBC spectrum of 2 showed the expected correlations in support of this structure as illustrated in Figure 1. Mochiquinone (1) is a unique structure in that it

^{*} To whom correspondence should be addressed. Tel.: (868) 662-5023. Fax: (868) 663-7741. E-mail: bmoot@tstt.net.tt.

† University of the West Indies.

^{*} University of Toronto.

Table 1. NMR Data of Mochiquinone (1)^a and the Corresponding Diacetate (2)^b

	1	2			
position	$\delta_{ m H}$ (mult, Hz)	δ_{C}	δ _H (mult, Hz)	¹H-¹H COSY	НМВС
1		185.17		·	· -
2		143.42°			
3		137.58⁵			
4		180.40			
5		148.98			
6		140.10			
2 3 4 5 6 7 8	3.06 (m)	30.52	3.03 (m)	1.20, 1.72	C-1, C-5, C-6, C-9, C-14
8	1.60 (m)	34.60	1.60 (m)	•	C-6, C-7, C-9, C-10
	1.78 (m)		1.72 (m)		C-6, C-7, C-10, C-14
9	(1.94) ^d (m)	26.48	(1.91) ^d (m)		C-7, C-8, C-10, C-11
10	5.02 (t, 6.9)	123.93	5.03 (t, 7)	1.54, 1.65	C-12, C-13
11		132.08			,
12	1.55 (s)	17.69	1.54 (s)	5.03	C-10, C-11, C-13
13	1. 6 8 (s)	25.70	1.65 (s)	5.03	C-10, C-11, C-12
14	1.17 (d, 7)	18.5 9	1.20 (d, 7)	3.03, 1.72	C-6, C-7, C-8
15	2.12 (s)	12.07	2.13 (s)	5.02	C-2, C-3, C-4
16	4.55 (br d)	57.02	5.02 (s)	2.13, 2.07	C-1, C-2, C-3, CO
aliphatic-OH	2.70 (br s)			-	
aromatic-OH	7.06 (s)				
CH_2OCOCH_3		170.47			
CH_2OCOCH_3		20.71	2.07 (s)	5.02	CO
$OCOCH_3$		168.01			
OCOCH3		20.40	2.34 (s)		CO

^a Recorded at 400 MHz in CDCl₃ with TMS as internal standard. ^b Recorded at 500 MHz in CDCl₃ with TMS as internal standard. ^c Carbons 2 and 3 were assigned on the basis of the expected effects of the α-CH₃ and -CH₂OAc groups. ^d Average value for an incompletely resolved -CH₂ group.

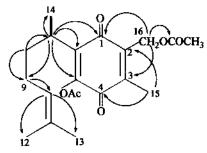


Figure 1. HMBC correlations (¹H → ¹³C) of compound 2.

is, as far as we are aware, the first sesquiterpene reported containing an additional C-alkylated group on the main skeleton.

Experimental Section

General Experimental Procedures. IR spectra were recorded on a PYE UNICAM SP3-200 spectrophotometer. UV spectra were measured on a HP 8452A diode array spectra spectrophotometer. HREIMS and EIMS were recorded on a KRATOS/AEI MS-50 spectrometer. ¹H and ¹³C NMR, COSY, HQSC, and HMBC spectra were recorded on either a Varian Unity 500 or a Bruker Avance DRX-400 spectrometer. Chemical shifts are given in & (ppm), and coupling constants expressed in hertz (Hz). Optical rotations were measured on a POLARTRONIC D polarimeter. Si gel 60 (70-230 mesh) was used for column chromatography, reversed-phase HPLC was carried out on a LDC/ Milton Roy Instrument System equipped with a refractomonitor III (Brownlee column RP₁₈, 250 \times 4.6 mm), and precoated Si gel plates (Kieselgel 60 F₂₅₄₊₃₃₈) were used for preparative TLC.

Animal Material. A sample of *P. rigida* was collected at a depth of 7 m from the Punta Aguirre coast in Mochima Bay, Sucre State, Venezuela, during August 1997. The organism was identified at the Institute of Marine Affairs, Trinidad (specimen no. IMA-1485).

Extraction and Isolation. The freshly collected organism was cut into pieces and immersed in MeOH (ca 2.0 L) at the collection site. After standing (2 days), the suspension was filtered and the residue further extracted with MeOH (1.5 L) for an additional 2 days. The total filtrate was concentrated to give an aqueous suspension, which was extracted with EtOAc (3 \times 250 mL), dried over anhydrous Na_2SO_4 , and evaporated to give a brown gum (9.4 g). This extract was subjected to Si gel (70-230 mesh) column chromatography, eluting with light petroleum and increasing concentrations of EtOAc. Two fractions eluting with 10-20% EtOAc in light petroleum on further purification by column chromatography and preparative TLC yielded a-curcumene (5.8 mg) and curcuphenol (21 mg), respectively. A later fraction, treated as above, was finally purified by reversed-phase HPLC using 40% aqueous MeOH to give (-)-curcuquinone (27.5 mg), while another fraction, on preparative TLC (C_6H_6 -acetone, 20:2, \times 2), gave a compound that quickly exidized to (-)-curcuquinene. Consequently, this fraction (28.0 mg) was acetylated with Ac₂O/pyridine at room temperature for 24 h to yield a mixture (27.2 mg), which was purified by preparative TLC (C₆H₆-acetone, 20:1) to afford (-)-curcuhydroguinone diacetate (11.2 mg). A fraction eluting with 40% EtOAc in light petroleum (102.0 mg) afforded an unstable yellow oil (1) after column chromatography on Si gel followed by preparative TLC (light petroleum-acetone, 3:1.

Mochiquinone (1): yellowish oil; IR (film) 3450, 3000-2820, 1650, 1630, 1450, 1390, 1372, 1200, 755 cm⁻¹; 1 H NMR data, see Table 1.

Acetylation of (1). Mochiquinone (9.0 mg) was treated with Ac₂O (0.5 mL) and pyridine (1 mL) and was allowed to stand at room temperature overnight. The solvent was removed in a stream of N₂ to give diacetate 2 (10.0 mg), which was purified by column chromatography on Si gel with light petroleum–EtOAc (5:1) to give a pale yellow oil; $[\alpha]_D$ –20.0° (c 0.10, CHCl₃); UV (MeOH) λ_{max} 296 nm; ¹H and ¹³C NMR data, see Table 1; EIMS m/z [M⁺] 362 (4),

320 (16), 260 (75), 191 (100), 178 (70); HREIMS m/z [M+] 362.1720 (calcd for $C_{20}H_{26}O_6$, 362.1729).

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