Pycnanthuquinone C, an Unusual 6,6,5-Tricyclic Geranyltoluquinone from the Western Australian Brown Alga *Cystophora harveyi*

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Chemical investigation of the Western Australian marine brown alga *Cystophora harveyi* resulted in the isolation of the new linearly fused 6,6,5-tricyclic compound pycnanthuquinone C (**1**), in addition to four previously reported geranyltoluquinol derivatives. Structures were elucidated by interpretation of spectrometric data. Compounds with the same cyclic skeleton as **1** have been reported to be useful drug leads for the treatment of type 2 diabetes, while compounds **4** and **7** are known constituents of Chinese medicinal herbs. A biosynthetic scheme encompassing all of the geranyltoluquinol derivatives isolated from *C. harveyi* is proposed.

Species of the brown algal genus *Cystophora* are restricted to the cool temperate waters of Australasia and are prominent members of inter- and subtidal rocky shore communities.[1−3] Previous chemical investigation of the more common members of the genus has resulted in the isolation of phlorotannins,[4−8] acyclic and cyclic geranyl and farnesylacetone derivatives, resorcinols, phloroglucinols, methylene-interrupted polyenes,[9−13] and two meroditerpenoids.[13] Several compounds isolated exhibit mild anti-inflammatory activity.[15,16] While numerous *Cystophora* species have extensive ranges along temperate Australasian coastlines, the waters of the southwest of Western Australia contain a number of endemic species, and it has been suggested that this area may be a site of active speciation within the genus.[2]

There has been only one published chemical investigation of *Cystophora* species from Western Australian waters, and thus, as part of an ongoing investigation into the diverse chemistry and chemotaxonomy of the *Cystophora* genus, a collection of *C. harveyi* Womersley (Cystoseiraceae) was made near Cape Leeuwin in Western Australia. Subsequent extraction and chromatographic separation resulted in the isolation of a novel geranyltoluquinone (**1**), containing a rare linearly fused 6,6,5-ring system, and four related compounds (**4**−**7**), three of which have been previously isolated from a Western Australian *Cystophora* sp.[17] Compounds **4** and **7** are known constituents of Asian medicinal herbs,[18,19] and this is the first report of **4** from a marine organism.

The crude acetone extract of *C. harveyi* was subjected to stepwise gradient separation on a silica gel Speedy column.[20] Further separation of the second Speedy column fraction over Sephadex LH-20 followed by centrifugal chromatography and normal-phase HPLC resulted in isolation of 3.2 mg of compound **1** as an optically active, yellow oil. High-resolution EIMS established the molecular formula as $C_{17}H_{22}O_4$ (found 290.1508, calcd 290.1518). The IR spectrum suggested the presence of hydroxyl groups (3356 cm^{-1}) and a conjugated ketone (1650 cm^{-1}), while maxima at 202.5 and 255.0 nm (log ϵ 4.03 and 3.65, respectively) in the UV spectrum are consistent with the presence of a *p*-quinone moiety.[17,21]

Carbon-13 NMR spectroscopy revealed the presence of seven quaternary, four methine, two methylene, and four methyl carbons (Table 1). Four of the downfield carbons were assigned as olefinic or aromatic carbons, and two signals, at δ_C 189.5 and 187.9, were attributed to two conjugated carbonyl carbons. As the molecular formula indicated the existence of seven double-bond equivalents, four of which must be due to olefinic and carbonyl bonds, compound **1** must be tricyclic.

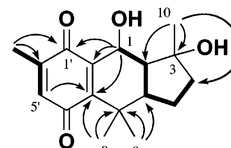

Figure 1. HMBC (arrows) and DQF-COSY (bold bonds) correlations for pycnanthuquinone C (**1**).

Table 1. NMR Spectroscopic Data (300 MHz, $CDCl_3$) for Pycnanthuquinone C (**1**)

position	δ_C, mult.	δ_H (*J* in Hz)	DQF-COSY	HMBC[a]
1	63.7, CH	5.11, d (4.3)	2	2, 6, 1′, 2′, 3′
2	46.7, CH	1.36, dd (13.9, 4.3)	1, 6	
3	80.3, qC			
4	40.6, CH_2	1.81, m	4b/5b, 5a	2, 3, 6
		1.55, m		
5	20.7, CH_2	1.88, m	4b/5b, 4a, 6	6
		1.54, m		4
6	43.5, CH	2.46, ddd (13.9, 7, 7)	2, 4b/5b, 5a	
7	38.1, qC			
8	19.5, CH_3	1.13, s		6, 7, 9, 3′
9	26.8, CH_3	1.34, s		6, 7, 8, 3′
10	26.5, CH_3	1.44, s		2, 3, 4
1′	189.5, qC			
2′	141.2, qC			
3′	151.5, qC			
4′	187.9, qC			
5′	135.5, CH	6.49, q (1.5)	6-′Me	1′, 3′, 6′-Me
6′	144.2, qC			
6′-Me	15.0, CH_3	1.99, d (1.5)	5′	1′, 5′, 6′
1-OH		4.05, bs[b]		
3-OH		3.25, bs[b]		

[a] HMBC correlations are from proton(s) stated to the indicated carbon. [b] D_2O exchangeable.

The HMBC spectrum of compound **1** showed a downfield methyl group (δ_H 1.99, 3H, d, 1.5 Hz, H-6′Me), which was correlated to a quaternary sp^2-hybridized carbon (δ_C 144.2, s, C-6′) and the carbonyl signal at δ_C 189.5 (C-1′), as well as having a long-range DQF-COSY correlation to H-5′ (δ_H 6.49, ^{1}H, q, 1.5 Hz). This was consistent with one side of the putative *p*-quinone moiety carrying a single methyl substituent (Figure 1). The unambiguous assignment of the remaining carbons in the *p*-quinone could be made from the observation of HMBC correlations between a downfield hydrogen on an sp^3 carbon external to the quinone (δ_H 5.11, ^{1}H, d, 4.3 Hz,

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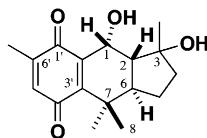

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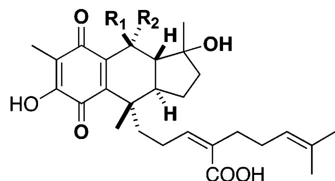
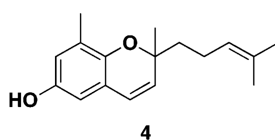


2 R_1 = H, R_2 = OH
3 R_1 = OH, R_2 = H



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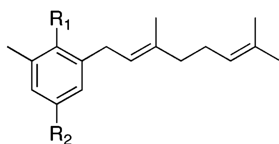
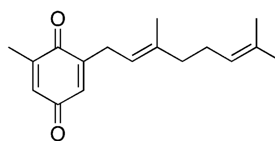


5 R_1 = OMe, R_2 = OH
6 R_1 = R_2 = OMe



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H-1) and C-1′, and two other carbons (δ_C 141.2, s, C-2′; 151.5, s, C-3′), whose relative disposition could be assigned from the observation of an HMBC correlation between H-5′ and C-3′.

Analysis of the gHMQC spectrum allowed the chemical shifts of H-2, H_2-4, and H_2-5 to be determined in the poorly resolved region of the proton spectrum (δ_H 1.3−1.9), leading to the ready establishment of the H-1, H-2, H-6, H_2-5, and H_2-4 proton spin system present in compound **1** by a DQF-COSY experiment. HMBC correlations between the protons of a singlet methyl group (δ_H 1.44, 3H, s, H-10) and a quaternary carbon (δ_C 80.3, s, C-3), C-2 and C-3, allowed the closure of the second ring in compound **1** between C-2 and C-4, via the quaternary carbon C-3, consistent with the singlet multiplicity of H_3-10. The HMBC correlations observed between the remaining two singlet methyl groups (δ_H 1.13, H_3-8; 1.34, H_3-9) and a quaternary carbon (δ_C 38.1, s, C-7) as well as carbons-6 and -3′, respectively, resulted in closing the final ring by linking C-3′ and C-6 through the geminal dimethyl at C-7. The carbon chemical shifts of C-1 and C-3 are typical of oxygen-bearing carbons, which, combined with the observation of two D_2O exchangeable protons at δ_H 3.25 and 4.05, indicates the presence of hydroxyl substituents at these positions, completing the planar structure of compound **1** as shown.

The large coupling constant between H-2 and H-6 (J = 13.9 Hz) led to the assignment of the ring junction as *trans*. Irradiation of the proton signal for H-1 resulted in an NOE of H-2, indicating they were on the same face of the molecule. These observations allowed the relative configuration of compound **1** to be partially assigned as 1*R**, 2*R**, 6*R**. When irradiated at H_3-8 the signals for H_3-9, H-2, and H-5b were enhanced, while small enhancements for the signals for H-5a and H_3-9 were observed when H-6 was irradiated. Unfortunately, NOE difference experiments were not helpful in ascertaining the orientation of substituents at C-3. Molecular modeling (MMFF) experiments using Spartan ’02 (Wavefunction, Inc., Irvine, CA) were conducted to see whether the compound **1** stereoisomers epimeric at C-3 have stable conformations that would produce ^{1}H, ^{1}H coupling constants sufficiently different to enable assignment of the configuration at this stereocenter. The most stable C-3 epimer conformations found were distinctive, having the orientation of C-4 “flapped” either up or down. While the resulting changes of the ^{1}H, ^{1}H dihedral angles from C-1 through C-6 suggest the 3*R** relative configuration at C-3, they were not of sufficient magnitude to produce an unequivocal assignment.

This is only the second report of a compound from this rare class of prenylated quinones with a linear 6,6,5-tricyclic skeleton. The previously reported antihyperglycemic compounds, pycnanthuquinones A and B (**2** and **3**, respectively), were isolated from the leaves and stems of the African plant *Pycnanthus angolensis*.[22,23] The magnitude of the coupling constant $J_{H-1,H-2}$ measured for compound **1** (J = 4.3 Hz) is comparable to that reported for pycnanthuquinone A (1*R**,2*R**,6*R**,7*S**; J = 3.6 Hz) but is only half that in pycnanthuquinone B (1*S**,2*R**,6*R**,7*S**), consistent with the relative configuration assigned for compound **1**. The trivial name pycnanthuquinone C is proposed for compound **1**.

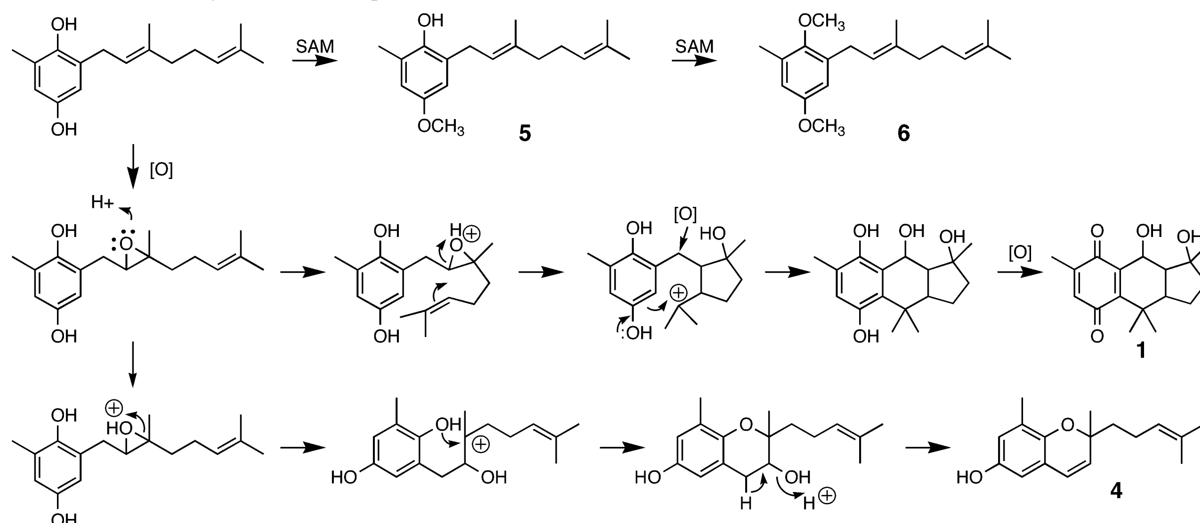
Compound **4** was obtained from the first Speedy column fraction as an optically active, dark orange-brown oil. Low-resolution EI mass spectrometry showed a molecular ion of *m/z* 258 consistent with the molecular formula $C_{17}H_{22}O_2$. The infrared spectrum suggested the presence of a hydroxyl group (3365 cm^{-1}), and an aromatic moiety was inferred from the presence of maxima at 217 and 264 nm (log ϵ 4.23 and 3.54, respectively) in the UV spectrum.

Carbon-13 NMR spectroscopy indicated the presence of 17 carbons: six quaternary, including an oxycarbon at δ_C 77.8, five methine, two methylene, and four methyl carbons. Easily discernible signals in the ^{1}H NMR spectrum were four aromatic or olefinic doublets at δ_H 6.46, 6.26, 6.23, and 5.56 (^{1}H each), a broad olefinic triplet at δ_H 5.09 (^{1}H), a D_2O exchangeable singlet at δ_H 4.65, and four methyl singlets at δ_H 2.12, 1.65, 1.56, and 1.35, the most downfield of which was consistent with an aromatic methyl group.

Examination of the NMR data suggested that **4** was a chromene derivative of a geranyltoluquinol. A subsequent search of the chemical literature resulted in the identification of **4** as atractylochromene, previously reported as an effective anti-inflammatory agent obtained from the rhizomes of the Chinese medicinal herb *Atractylodes lancea*.[18] The isolation of atractylochromene from *C. harveyi* is the first report of this compound from a marine organism.

Compounds **5**−**7** were all isolated as pale yellow oils. Mass spectral and NMR data were consistent with these compounds being geranyltoluquinol derivatives, and structural interpretation was confirmed by comparison with published data,[17] resulting in their assignment as (2′*E*)-2-(3′,7′-dimethylocta-2′,6′-dienyl)-4-hydroxy-1-methoxy-6-methylbenzene (**5**), (2′*E*)-1,4-dimethoxy-(3′,7′-dimethylocta-2′,6′-dienyl)-6-methylbenzene (**6**), and (2′*E*)-2-(3′,7′-dimethylocta-2′,6′-dienyl)-6-methyl-2,5-cyclohexadiene-1,4-dione (**7**). The initial report of compounds **5**−**7** did not provide a species name for the source alga. Subsequent inquiries revealed that this species was in fact *C. harveyi*.[24] The published ^{13}C NMR data for **5**−**7** contain a number of acknowledged ambiguities due to lack of availability of 2D NMR experiments. Ready access to HMQC and HMBC experiments in this study resolved these ambiguities (see the Experimental Section). It should be noted that, as pointed out by Capon et al.,[17] alkylated toluquinols are known to oxidize readily in air, and it is possible that compound **7** may be

Scheme 1. Postulated Biosynthesis of Compounds **1** and **4**−**6**



an artifact of the extraction and isolation process (e.g., the actual *C. harveyi* metabolite is the corresponding quinol).

The isolation of five compounds of the same structural class from a single source organism suggests that they may be derived from a common precursor (Scheme 1). If the precursor of **7** occurs naturally as a quinol, the two methoxy derivatives **5** and **6** could be the result of methylation by S-adenosyl methionine (SAM). The formation of chromene **4** could result via the biosynthetic equivalent of epoxidation of the 2,3-double bond, followed by opening of the epoxide, attack at the resulting C-3 tertiary carbocation by the C-1′ phenol to form the cyclic ether, and, finally, facile dehydration of the resulting secondary alcohol to form the benzylic double bond. The proposed biosynthesis of the tricyclic quinone **1** is the result of an alternative opening of the 2,3-epoxy intermediate. The epoxide may be opened by the attack of the π-electrons of the 6,7-double bond at C-2, resulting in the formation of a cyclopentyl tertiary carbocation. The C-7 carbocation is then open to aromatic electrophilic substitution to form the final tricyclic structure. Subsequent oxidation of the quinol leads to **1**.

Surprisingly for such a relatively simple group of compounds, a search of the chemical literature revealed that geranyltoluquinol compounds with a methyl substitution at C-6′ (such as **5**−**7**) appear to be restricted to *C. harveyi* and the terrestrial plant genera *Atractylodes*[18] and *Atractylis*.[19] Species from both of these plant genera are commonly used in traditional Asian medicine. For example, a decoction of the rhizomes of *Atractylodes lancea* (which contains atractylochromene, **4**) is traditionally used for the treatment of rheumatic diseases, digestive disorders, mild diarrhea, and influenza. Resch et al.[18] reported that atractylochromene inhibits the 5-LOX (IC_{50} 3.3 μM) and COX-1 (IC_{50} 0.6 μM) enzymes, which are essential for the metabolism of arachidonic acid to prostaglandins, thromboxanes, or leukotrienes, all of which play a central role in the regulation of pain, inflammation, and hypersensitivity. The rhizomes of the Korean medicinal herb *Atractylis koreana* (which contains **7**) are used to treat dysentery, fever, arthritis, and apoplexia. The compounds isolated from *C. harveyi* are similar to the known cytotoxic substances (e.g., verapliquinone A) reported from a number of ascidians,[25,26] the notable difference being the presence of a 6′-methyl group in the *C. harveyi* compounds.

Pycnanthuquinones A and B significantly reduced plasma glucose concentrations when fed orally to hyperglycemic mice, and this was further linked to the compounds actually controlling insulin-stimulated glucose uptake.[22] These compounds are reported to be useful leads for the development of new drugs for the treatment of type 2 diabetes, although no follow-up reports have appeared. Compound **1** is the only other known compound from the pycnanthuquinone structure class and may also be a useful tool in probing the biochemistry of type 2 diabetes and in producing a new, small molecule chemotherapy for this disease.

C. harveyi appears to be a rich source of geranyltoluquinols, making this species unique among the members of the *Cystophora* genus, which are known to produce geranylgeranyltoluquinols, phloroglucinols, resorcinols, and farnesylacetone derivatives.[4−14] The presence of compounds in *C. harveyi* that are known to be, or are structurally related to, biologically active compounds from medicinal plants suggests that this alga may be a potential source of useful medicinal compounds.

Experimental Section

General Experimental Procedures. Optical rotations were recorded in $CHCl_3$ on a Perkin-Elmer 241 polarimeter. UV spectra were recorded as ethanolic solutions on a Hitachi U-2000 UV−visible spectrometer. IR spectra were recorded as casts on NaCl plates using a Perkin-Elmer Paragon 1000 FT-IR spectrometer. NMR data were collected with a Bruker Avance 300 DPX NMR spectrometer and with solvent ($CDCl_3$) signals as an internal calibration standard (δ_H 7.24, residual ^{1}H, δ_C 77.0) utilizing standard Bruker pulse programs. HREIMS was performed by Dr. Noel Davies and Mr. Marshall Hughes of the Central Science Laboratories, University of Tasmania, Hobart, Australia, on a Kratos Concept IQ mass spectrometer with 70 eV ionization and 5.3 kV accelerating voltage. Low-resolution MS were obtained using a Shimadzu GC-17A gas chromatograph coupled to a Shimadzu QP5050A quadrapole mass spectrometer. Solvents used for extraction or initial chromatography were distilled from glass; HPLC or spectroscopic grade solvents were used on all other occasions. Light petrol was the 60−80 °C boiling fraction of supplied bulk "mixed hexanes". Gel permeation chromatography was conducted with Sephadex LH-20 using a column 35 mm i.d. × 700 mm. Speedy column chromatography[20] utilized Merck silica gel H (20−25 μm), and centrifugal chromatography employed a chromatotron (Harrison Research); the stationary phase was Merck silica gel 60 F_{254} containing gypsum. All semipreparative HPLC was normal phase and accomplished utilizing a Waters 600 controller and a Waters PDA detector with a Phenomenex Luna 10 μm silica 100A (250 × 10 mm) semipreparative column at a flow rate of 3.5 mL/min.

Plant Material. *Cystophora harveyi* was collected by scuba (ca. 5 m depth) from the first bay to the east of the Cape Leeuwin lighthouse, Western Australia (33°22′ S, 115°08′ E) in November 1998. The specimen exhibited the characteristic habit of the species, and the initial field identification was verified by Dr. John Huisman of the School of Biological Sciences and Biotechnology, Murdoch University, Western Australia. A voucher specimen is maintained in the Murdoch University Herbarium, Western Australia (MURUAA981104004). Bulk material was frozen at −4 °C until return to The University of Newcastle, where it was stored at −20 °C until required.

Extraction and Isolation. The frozen alga was extracted with acetone (×4), the solvent evaporated under vacuum, and the residual

aqueous phase extracted with diethyl ether. The organic phase was dried with anhydrous $MgSO_4$, and the resulting crude extract subjected to gradient Speedy column chromatography in 10% steps from light petrol to $CHCl_3$ to EtOAc. Like fractions (by TLC) were combined to give four Speedy column fractions. A portion of the first Speedy column fraction was separated over Sephadex LH-20 with MeOH/$CHCl_3$ (1:1), and the fractions containing lower molecular weight compounds (ca. <600 amu) were further partitioned on Sephadex LH-20 by light petrol/$CHCl_3$/EtOH (10:10:1). Subsequent purification by centrifugal chromatography using Et_2O/light petrol (gradient 1:49 to 1:19) yielded compounds **6** [180 mg, R_f 0.50 (Et_2O/light petrol, 1:3), 0.03%, based upon dry extracted weight of alga] and **7** [68 mg, R_f 0.42 (Et_2O/light petrol, 1:3), 0.01%]. A second portion of the first Speedy column fraction was simply separated by centrifugal chromatography using Et_2O/light petrol (1:4), yielding pure **4** [73 mg, R_f 0.38 (Et_2O/light petrol, 1:5), 0.01%] and **5** [58 mg, R_f 0.46 (Et_2O/light petrol, 2:3), 0.01%]. The second Speedy column fraction was separated over Sephadex LH-20 with MeOH/$CHCl_3$ (1:1) to yield five fractions, the third of which was subjected to gradient centrifugal chromatography eluting with MeOH/$CHCl_3$ (1:99 to 1:1) and further purification by semipreparative HPLC (isooctane/$CHCl_3$/EtOH, 50:49:1) to yield **1** [3.2 mg, R_f 0.28 (light petrol/$CHCl_3$/EtOH, 10:10:1), 0.0005%].

Pycnanthuquinone C (1): yellow oil; $[\alpha]^{21}_D$ +41 (*c* 0.16, $CHCl_3$); UV (EtOH) λ_{max} (log ϵ) 202.5 (4.03), 255.0 (3.65); IR (neat) ν_{max} 3356.2 (br, OH), 2963.7, 1650.2 (s, C=O), 1458.2, 1379.2, 1252.8, 1167.9, 1090.5, 980.8, 934.0, 891.2, 814.2, 754.9, 667.8 cm^{-1}; ^1H and ^{13}C NMR, see Table 1; difference ^1H, ^1H NOE spectroscopy (300 MHz, $CDCl_3$), H-irradiated: H-enhanced (%) H-1: H-2 (0.6); H-6: H-5a, H-9 (2.4); H-8: H-2 (3.4), H-5b (1.0), H-9: EIMS *m/z* 290 [M$^+$] (<1), 288 (1), 272 (5), 257 (11), 214 (61), 201(100), 187 (14), 171 (14), 133 (11), 105 (9), 85 (54), 83 (53), 69 (13), 57 (11), 55 (15), 47 (26), 43 (88); HREIMS *m/z* 290.1508 (calcd 290.1518 for $C_{17}H_{22}O_4$).

Atractylochromene (4): orange-brown oil; $[\alpha]^{21}_D$ −3 (*c* 0.2, $CHCl_3$); UV (EtOH) λ_{max} (log ϵ) 217.0 (4.23), 264.0 (3.54); IR (neat) ν_{max} 3365, 2913, 1591, 1464, 1215 cm^{-1}; ^1H and ^{13}C NMR agreed with published values;[18] EIMS *m/z* 258 [M$^+$] (19), 243 (6), 215 (2), 175 (100), 161 (3), 145 (4), 131 (4), 105 (3), 91 (9), 77 (7), 69 (21), 53 (7), 41 (40).

(2′*E*)-2-(3′,7′-Dimethylocta-2′,6′-dienyl)-4-hydroxy-1-methoxy-6-methylbenzene (5): yellow-orange oil; IR ν_{max} (neat) 3383, 2921, 1727 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.47 (^1H, s, H-5′), 6.46 (^1H, s, H-3′), 5.25 (^1H, tq, *J* = 7.2, 1.1 Hz, H-2), 5.08 (^1H, tm, *J* = 6.7, 1.3 Hz, H-6), 4.48 (^1H, bs, 1′-O*H*), 3.66 (3H, s, 1′-OC*H*$_3$), 3.30 (2H, d, *J* = 7.2 Hz, H-1), 2.23 (3H, s, 6′-C*H*$_3$), 2.09 (2H, m, H-5), 2.04 (2H, m, H-4), 1.69 (3H, bs, 3-C*H*$_3$), 1.66 (3H, bs, 7_{trans}-C*H*$_3$), 1.58 (3H, bs, 7_{cis}-C*H*$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 151.4 (C, C-4′), 150.4 (C, C-1′), 136.3 (C, C-3), 135.7 (C, C-2′), 132.0 (C, C-6′), 131.5 (C, C-7), 124.3 (CH, C-6), 122.6 (CH, C-2), 115.1 (CH, C-5′), 113.8 (CH, C-3′), 60.5 (CH_3, C-1′O*C*H$_3$), 39.7 (CH_2, C-4), 28.0 (CH_2, C-1), 26.6 (CH_2, C-5), 25.7 (CH_3, C-7_{trans}CH$_3$), 16.1* (CH_3, C-7_{cis}CH$_3$), 16.2* (CH_3, C-6′*Me*), 15.5 (CH_3, C-3*Me*) (*may be interchanged); EIMS *m/z* (%) 274 [M]$^+$ (13), 259 (1), 243 (2), 231 (6), 218 (<1), 205 (20), 190 (11), 175 (15), 163 (10), 151 (25), 137 (21), 123(58), 107 (6), 91 (13), 81 (16), 77 (15), 69 (59), 55 (21), 41 (100).

(2′*E*)-1,4-Dimethoxy-(3′,7′-dimethylocta-2′,6′-dienyl)-6-methylbenzene (6): yellow-orange oil; IR ν_{max} (neat) 1599, 1480, 1222, 1062, 1013 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.58 (2H, bs, H-3′,5′), 5.32 (^1H, bt, *J* = 7.0 Hz, H-2), 5.12 (^1H, bt, *J* = 6.6 Hz, H-6), 3.75 (3H, s, 4′-OC*H*$_3$), 3.70 (3H, s, 1′-OC*H*$_3$), 3.37 (2H, bd, *J* = 6.9 Hz, H-1), 2.30 (3H, s, 6′-C*H*$_3$), 2.12 (2H, m, H-5), 2.08 (2H, m, H-4), 1.74 (3H, s, 3-C*H*$_3$), 1.69 (3H, 7_{trans}-C*H*$_3$), and 1.61 (3H, s, 7_{cis}-C*H*$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 155.5 (C, C-4′), 150.4 (C, C-1′), 136.2 (C, C-3), 135.4 (C, C-2′), 131.6 (C, C-6′), 131.4 (C, C-7), 124.2 (CH, C-6), 122.8 (CH, C-2), 113.5 (CH, C-5′), 112.7 (CH, C-3′), 60.4 (CH_3, C-1′O*C*H$_3$), 55.3 (CH_3, C-4′O*C*H$_3$), 39.7 (CH_2, C-4), 28.2 (CH_2, C-1), 26.6 (CH_2, C-5), 25.6 (CH_3, 7_{trans}-*C*H$_3$), 17.6 (CH_3, 7_{cis}-*C*H$_3$), 16.3 (CH_3, C-6′*C*H$_3$), 16.1 (CH_3, C-3*C*H$_3$); EIMS *m/z* (%) 288 [M]$^+$ (34), 273 (1), 257 (4), 245 (6), 219 (34), 204 (16), 189 (24), 188 (24), 173 (12), 166 (28), 165 (34), 151 (35), 135 (20), 123 (61), 105 (9), 91 (16), 81 (17), 69 (63), 55 (19), 41 (100).

(2′*E*)-2-(3′,7′-Dimethylocta-2′,6′-dienyl)-6-methyl-2,5-cyclohexadiene-1,4-dione (7): yellow oil; IR ν_{max} (neat) 1652 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.52 (^1H, dq, *J* = 2.7, 1.5 Hz, H-5′), 6.44 (^1H, dt, *J* = 2.6, 1.7 Hz, H-3′), 5.12 (^1H, tq, *J* = 7.3, 1.2 Hz, H-2), 5.05 (^1H, bm, H-6), 3.10 (2H, d, *J* = 7.3 Hz, H-1), 2.07 (2H, m, H-5), 2.05 (2H, m, H-4), 2.03 (3H, s, H-6′C*H*$_3$), 1.66 (3H, H-7_{trans}C*H*$_3$), 1.59 (3H, s, H-3C*H*$_3$), 1.57 (3H, s, H-7_{cis}C*H*$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 188.03 (C, C-1′), 187.98 (C, C-4′), 148.5 (C, C-2′), 145.9 (C, C-6′), 139.8 (C, C-3), 133.1 (CH, C-5′), 132.2 (CH, C-3′), 131.8 (C, C-7), 123.9 (CH, C-6), 118.0 (CH, C-2), 39.6 (CH_2, C-4), 27.5 (CH_2, C-1), 26.4 (CH_2, C-5), 25.7 (CH_3, 7_{trans}-*C*H$_3$), 17.7 (CH_3, 7_{cis}-*C*H$_3$), 16.05 (CH_3, C-3*C*H$_3$), 15.99 (CH_3, C-6′*C*H$_3$); EIMS *m/z* (%) 258 [M]$^+$ (7), 243 (2), 215 (2), 189 (1), 175 (100), 161 (2), 137 (2), 121 (4), 91 (7), 77 (7), 69 (18).

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