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TETRAPRENYLTOLUQUINOL DERIVATIVES FROM THE BROWN ALGA *CYSTOSEIRA ZOSTEROIDES*

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Key Word Index—*Cystoseira zosteroides*; Cystoseiraceae; brown algae; tetraprenyltoluquinols.

Abstract—From the brown alga *Cystoseira zosteroides* five new tetraprenyltoluquinols have been isolated and their structures determined by spectral analysis.

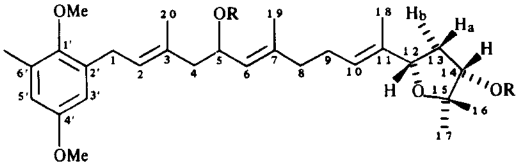
INTRODUCTION

As part of a phytochemical study of the Mediterranean brown algae belonging to the genus *Cystoseira* [1–6], we have examined *C. zosteroides* (Turner) C. Agardh, a deep-water species characterized by oblong or cylindrical, smooth tophules and receptacles at the base of secondary branches; the last morphological attribute makes it unique among the *Cystoseira* species.

RESULTS AND DISCUSSION

Examination by TLC of the dichloromethane extract of the alga revealed the presence of five secondary metabolites, which were separated and purified by chromatographic procedures.

The major secondary metabolite of *C. zosteroides*, zosterdiol A(**1**), $[\alpha]_D + 0.5°$, had molecular formula $C_{29}H_{44}O_5$ (HREIMS) and displayed UV absorptions at 222 and 281 nm ($\varepsilon = 13\,800$ and 3200), indicative of a hydroquinol chromophore. The IR spectrum presented hydroxyl (3460 cm^{-1}) and aromatic (1605, 1595 cm^{-1}) bands, and verified the absence of carbonyl functions. The existence of a 2,5-dimethoxy-3-methylbenzyl moiety was suggested by a base peak at m/z 165 in the mass spectrum of **1** and confirmed by the appropriate resonances in the ^{13}C and ^{1}H NMR spectra (Table 1). The presence of two secondary alcohol functions in the molecule was established by acetylation with the formation of the diacetate **2**, whose ^{1}H NMR spectrum exhibited two acetoxymethyl signals at $\delta 2.07$ and 1.94. The carbinolic protons appeared at δ 5.66 and 5.00 showing downfield shifts of $\delta 1.21$ and 1.12, respectively. The last oxygen atom was assigned to a heterocycle formed by an ether bridge linking the remaining two sp^3 oxygen-bearing carbons. Careful examination of proton–proton couplings, both direct and long range, allowed us to define the whole proton sequence in the diterpenoid side chain. One-bond heteronuclear correlation [7–9] permitted the assignment of all the protonated carbons in the ^{13}C NMR spectrum of **1**, in particular those contributed by the secondary alcohol functions ($\delta 66.2$, C-5 and 78.3, C-14). This determined univocally the nature of the heterocyclic ring and, consequently, zosterdiol A was formulated as **1**. Assignment of the quaternary carbons was possible by the application of long-range ^{1}H–^{13}C shift correlation spectroscopy [10] (Table 1), which also furnished supplementary evidence for the validity of structure **1** for zosterdiol A.



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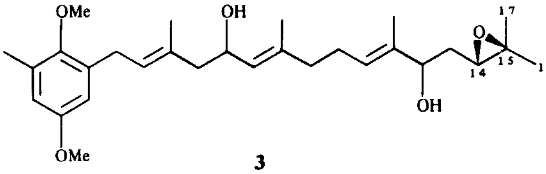

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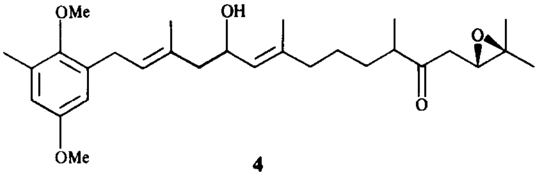

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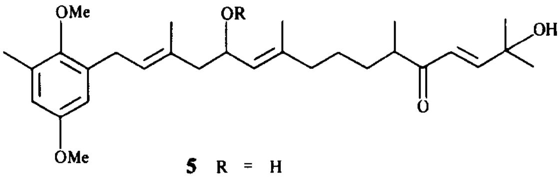

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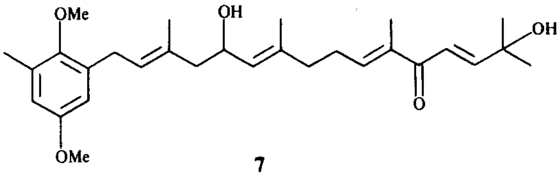

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Table 1. ^{1}H and ^{13}C NMR data of **1** (^{1}H and ^{13}C NMR 250 and 62.9 MHz, respectively, $CDCl_3$, TMS as int. standard)

Position	δ^{13}C	DEPT	δ^{1}H J_{HH}	*Long range correlation
1′	150.3	C		6′-Me, 1′-OMe, H-3′, H-5′, 2H-1
2′	134.8	C		2H-1
3′	112.7	CH	6.54 *br s*	H5′, 2H-1
4′	155.5	C		4′-OMe, H-3′, H-5′
5′	113.7	CH	6.54 *br s*	6′-Me, H-3′
6′	131.6	C		6′-Me
1	28.6	CH_2	3.35 *d* (7)	H-3′
2	126.3	CH	5.37 *t* (7)	2H-1, 3H-20, 2H-4
3	132.6	C		2H-1, 3H-20, 2H-4
4	47.8	CH_2	2.17 *m*	H-2, 3H-20
5	66.2	CH	4.45 *ddd* (8.5, 8, 5.2)	
6	128.5	CH	5.14 *d* (7.5)	2H-4, 3H-19
7	137.1	C		2H-8, 3H-19
8	38.9	CH_2	2.03 *m*	H-6, 2H-9, 3H-19
9	25.3	CH_2	2.18 *m* 2.05 *m*	
10	124.4	CH	5.50 *t* (7)	2H-9, H-12, 3H-18
11	136.4	C		2H-9, 3H-18, H_B-13
12	79.7	CH	4.30 *t* (7)	3H-18
13	39.1	CH_2	H_A 2.40 *m* H_B 1.80 *m*	
14	78.3	CH	3.88 *br t* (3.5)	H_B-13, 3H-16, 3H-17
15	83.0	C		H_A-13, 3H-16, 3H-17
16	26.0	CH_3	1.18 *s*	3H-17
17	22.5	CH_3	1.29 *s*	3H-16
18	12.3	CH_3	1.59 *s*	H-10, H-12
19	16.0	CH_3	1.61 *s*	H-6
20	16.4	CH_3	1.76 *s*	H-2, 2H-4
1′-OMe	60.2	CH_3	3.66 *s*	
4′-OMe	55.2	CH_3	3.72 *s*	
6′-Me	16.3	CH_3	2.23 *s*	H-5′

*Long range correlations were obtained with maximum polarization transfer for $J = 10$ Hz.

The high field position of the vinyl methyls at C-3, C-7 and C-11 in the ^{13}C NMR spectrum of **1** indicated the *E*-geometry of the relevant double bonds. The relative stereochemistry at the chiral centres at C-12 and C-14 was determined to be as depicted from the NOESY spectrum [11], which showed H-12 and H-14 to be on the same face of the tetrahydrofuran ring.

Another of the new metabolites isolated from *C. zosteroides*, zosterdiol B (**3**), was an isomer of **1**, $[\alpha]_D + 1.1°$, ν_{max} 3410 (OH) and 1610 cm^{-1} (aromatic), λ_{max} 222 and 284 nm ($\varepsilon = 12000$ and 3000). A base peak at *m/z* 165 in the mass spectrum of **3** was indicative of the same benzenoid moiety as in **1**; this was confirmed by comparison of the ^{1}H and ^{13}C NMR features of **3** (Tables 2 and 3) with those of **1**, which also established the identity of a large portion of the side chain involving C-1–C-9 and including the secondary alcohol function at C-5 (^{1}H NMR: δ4.46, *m*, C<u>H</u>OH; ^{13}C NMR: 65.9, *d*, CHOH). The ^{13}C NMR spectrum contained two signals whose chemical shifts (δ61.7, *d* and 58.3 *s*) are fairly characteristic for epoxy carbons; this and signals in the ^{1}H NMR spectrum for an oxirane proton signal (δ2.86, *dd*) and two methyls on quaternary oxygen-bonded carbon (δ1.26 and 1.30), were consistent with the presence of a terminal epoxy moiety. The last oxygen was contributed by a secondary alcohol function (δ4.20, *dd*, sharpened after addition of D_2O, C<u>H</u>OH), whose position was inferred by the fact that the methylene protons at C-13 (δ1.60 and 1.87) were found to be homonuclearly coupled (COSY) [12, 13] to both H-12 and H-14. On the evidence above, zosterdiol B was confidently assigned structure **3**. A difference NOE experiment assessed that the methyl resonating at δ1.34 and H-14 are on the same side of the oxirane ring.

The third compound isolated, zosteronol (**4**), $C_{29}H_{44}O_5$, $[\alpha]_D + 1.5°$, displayed IR absorptions for hydroxyl (3470 cm^{-1}), unconjugated ketone (1715 cm^{-1} and benzenoid (1610, 1600 cm^{-1}) functions, while the UV spectrum indicated the same benzenoid chromophore as in the metabolites described above (λ_{max} 222 and 282 nm, $\varepsilon = 10000$ and 2600). The ^{1}H and ^{13}C NMR spectra of zosteronol (Tables 2 and 3) showed several features in common with zosterdiol A and B, illustrating the aromatic unit and the first two isoprenoid units of the side chain, which could be easily expanded by decoupling experiments to include carbons C-9–C-11. Taking into account the presence of a terminal oxirane ring (^{1}H NMR: δ3.09, *t*, H-14; 1.34 *s*, Me-16 and 1.24 *s*, Me-17.

Table 2. ^{13}C NMR assignments for compounds **3**, **4**, **5** and **7** (62.5 MHz, $CDCl_3$, TMS as int. standard)*

Position	**3**	**4**	**5**	**7**
1′	150.3 *s*	150.3 *s*	150.5 *s*	150.4 *s*
2′	134.8 *s*	134.8 *s*	134.8 *s*	134.7 *s*
3′	112.7 *d*	112.7 *d*	112.9 *d*	112.9 *d*
4′	155.5 *s*	155.5 *s*	155.6 *s*	155.5 *s*
5′	113.7 *d*	113.7 *d*	113.8 *d*	113.7 *d*
6′	131.9 *s*	131.8 *s*	131.8 *s*	131.9 *s*
1	28.8 *t*	28.8 *t*	28.8 *t*	29.0 *t*
2	127.0 *d*	126.9 *d*	126.9 *d*	127.3 *d*
3	132.4 *s*	132.4 *s*	132.4 *s*	132.2 *s*
4	48.1 *t*	48.1 *t*	48.1 *t*	48.1 *t*
5	69.9 *d*	65.9 *d*	66.2 *d*	65.9 *d*
6	127.8 *d*	127.6 *d*	127.9 *d*	128.6 *d*
7	137.3 *s*	137.7 *s*	137.5 *s*	137.8 *s*
8	38.8 *t*	39.2 *t*	38.8 *t*	38.0 *t*
9	25.5 *t*	25.0 *t*	24.5 *t*	26.7 *t*
10	126.0 *d*	32.0 *t*	32.1 *t*	142.7 *d*
11	116.1 *s*	46.4 *d*	44.3 *d*	136.6 *s*
12	75.5 *d*	212.0 *s*	203.9 *s*	192.9 *s*
13	34.1 *t*	40.9 *t*	124.1 *d*	121.3 *d*
14	61.7 *d*	59.3 *d*	152.5 *d*	152.4 *d*
15	58.3 *s*	58.0 *s*	70.7 *s*	71.0 *s*
16	24.7 *q*	24.5 *q*	29.3 *q*	29.3 *q*
17	18.9 *q*	18.8 *q*	29.4 *q*	29.4 *q*
18	11.5 *q*	16.2 *q*	15.8 *q*	11.7 *q*
19	16.5 *q*	16.4 *q*	16.3 *q*	15.3 *q*
20	16.4 *q*	16.3 *q*	16.4 *q*	16.3 *q*
6′-Me	16.3 *q*	16.4 *q*	16.4 *q*	16.3 *q*
1′-OMe	60.4 *q*	60.4 *q*	60.3 *q*	60.4 *q*
4′-OMe	55.4 *q*	55.3 *q*	55.3 *q*	55.4 *q*

*Assignments have been aided by direct and long-range ^1H–^{13}C correlation spectroscopy.

^{13}C NMR: 59.3, *d*, C-14 and 58.0 *s*, C-15), determination of the remaining part of the side chain was trivial and the new metabolite was allocated structure **4**.

Another of the *C. zosteroides* metabolites, zosterondiol A (**5**), $[\alpha]_D + 0.7°$, $C_{29}H_{44}O_5$, exhibited hydroxyl (3440 cm^{-1}) and enone (1670 and 1630 cm^{-1}) bands in the IR spectrum, and benzenoid (222 and 280 nm, $\varepsilon = 18000$ and 2600) and enone (234 nm, $\varepsilon = 11700$) absorptions in the UV spectrum. An intense peak at *m/z* 165 in the mass spectrum revealed the presence of a 2,5-dimethoxy-3-methylbenzyl moiety. Acetylation of **5** gave a monoacetate (**6**) which retained hydroxyl absorption in the IR spectrum. In the light of this information, the three oxygen atoms in the side chain were assigned to a secondary hydroxyl (^{1}H NMR: δ4.48, *m*; ^{13}C NMR: 66.2, *d*, CHOH), a tertiary hydroxyl and a conjugated carbonyl. These features suggested that zosterondiol A could be the 4′-methyl ether of a compound isolated from *C. elegans* by Banaigs *et al.* [14]. In fact, zosterondiol A had ^{1}H and ^{13}C NMR spectra (Tables 2 and 3) closely comparable with the *C. elegans* metabolite, apart from the obvious presence of the resonances associated with the 4′-methoxyl (incidentally, on the basis of direct and long-range heteronuclear correlation experiments the assignments of a couple of protons, H-13, -14, and two pairs of carbons, C-3, -7 and C-13, -14, have been each reversed with respect to those of the French workers).

The structure of the last metabolite from *C. zosteroides*, zosterondiol B (**7**), $[\alpha]_D + 0.9°$, ν_{max} 3440 cm^{-1} (OH) and 1665 cm^{-1} (conjugated carbonyl), λ_{max} 222 ($\varepsilon = 10800$), 254 ($\varepsilon = 9200$) and 284 ($\varepsilon = 2800$), was readily established by comparison of its spectral properties with those of **5**. The ^{13}C NMR spectrum of **7** differed from that of **5** by the replacement of a methine (δ44.3) and a methylene (δ32.1) resonance with a pair of olefinic signals at δ142.7 and 136.6. The concomitant downfield shift of the resonance for the carbonyl carbon from δ203.9 in **5** to 192.9 in zosterondiol B showed that the additional double bond was conjugated to the carbonyl, thus leading unambiguously to structure **7** for the new algal metabolite.

EXPERIMENTAL

General experimental procedures. ^{1}H and ^{13}C NMR: 250 and 62.9 MHz, respectively. Chemical shifts are given in δ values (ppm) with TMS as int. standard. MS: direct inlet, 70 eV. Final purification of all metabolites was achieved by PLC on silica gel (LiChrosorb Si-60, 25–40 μ) using a Jobin–Yvon Miniprep liquid chromatograph. TLC was carried out using glass-backed precoated silica gel F_{254} plates (Merck). Compounds were detected by spraying with 10% soln of $Ce(SO_4)_2$ in 1 M H_2SO_4, or by UV light (254 nm). All solvents were spectral grade or distilled prior to use.

Plant material. Cystoseira zosteroides (Turner) C. Agardh was collectd by hand using SCUBA (−20 m) at Aci Castello (Catania) in May 1987. A voucher specimen was deposited in the Herbarium of the Department of Botany, Catania, Italy.

Extraction and purification. Shade-dried and ground plant material (400 g) was extracted (× 3) with CH_2Cl_2 at room temp. with continuous stirring. The combined extracts were evapd *in vacuo* to yield the final crude residue as a dark green oil (9.5 g) which was chromatographed on a Jobin–Yvon Chromatospac prep. LC (Kieselgel 60; increasing concentrations of Et_2O in hexane as the eluent). Fractions of 250 ml were collected and those exhibiting similar TLC profiles combined. Fractions 22 and 23 were subjected to prep. LC using CH_2Cl_2–Et_2O (19:1) as the eluant to give pure **4** (52 mg, 0.013% dry wt of the alga). Prep. LC (CH_2Cl_2–dioxane, 49:1) of fractions 38 and 39 gave a mixture of **1** and **5**, which was separated by further chromatography (Et_2O–hexane, 7:3) to yield pure **1** (312 mg, 0.078% dry wt) and **5** (48 mg, 0.012% dry wt). Fraction 40 was purified by successive prep. LC using as solvents CH_2Cl_2–dioxane (97:3) and then Et_2O–hexane (3:1) to give **3** (24 mg, 0.0067% dry wt). Finally, fractions 41 and 42 were subjected to prep. LC with CH_2Cl_2–dioxane (93:7), followed by prep. LC with Et_2O–$i$$Pr_2O$ (3:2) to yield **7** (8 mg, 0.002% dry wt). All compounds were obtained as oils.

Zosterdiol A (**1**). $[\alpha]_D^{20}$: +0.5° (EtOH; *c* 2.0); IR ν_{max}^{film} cm^{-1}: 3460, 1605, 1595; UV λ_{max}^{EtOH} nm: 222 ($\varepsilon = 13800$), 281 ($\varepsilon = 3200$); HRMS: $[M - H_2O]^+$ 454.3098 (calc. for $C_{29}H_{42}O_4$ 454.3083); MS *m/z* (rel. int.): 454 (5), 436 (3), 410 (8), 368 (5), 285 (12), 253 (20), 220 (60), 205 (24), 187 (24), 165 (100), 137 (25), 121 (20), 107 (15), 95 (10), 81 (20), 71 (55), 43 (20), 41 (12).

Zosterdiol A acetate (**2**). Acetylation of **1** (Ac_2O–pyridine, overnight at room temp.) and conventional work-up gave the acetate **2**, oily; IR ν_{max}^{film} cm^{-1}: 1745, 1610, 1485; ^{1}H NMR: δ6.54 and 6.51 (2H, AB system, $J = 3$ Hz, H-5′ and H-3′), 5.66 (1H, *m*, H-5), 5.40 (1H, *t*, $J = 7$ Hz, H-10), 5.32 (1H, *t*, $J = 7$ Hz, H-2), 5.11 (1H, *d*, $J = 8$ Hz, H-6), 5.00 (1H, *dd*, $J = 5$ and 7 Hz, H-14), 4.32 (1H, *t*, $J = 7$ Hz, H-12), 3.73 (3H, *s*, 4′-OMe), 3.66 (3H, *s*, 1′-OMe), 3.31 (2H, *d*, $J = 7$ Hz, H-1), 2.48 (1H, *m*, Ha-13), 2.26 (3H, *s*, 6′-

Table 3. ^{1}H NMR of compounds **3**, **4**, **5** and **7** (250 MHz, $CDCl_3$, TMS as int. standard)*

	Compound			Compound	
Position	**3**	**4**	Position	**5**	**7**
H-3′	6.53 AB (3)	6.53 AB (3)	H-3′	6.52 AB (3)	6.51 AB (3)
H-5′	6.55	6.55	H-5′	6.55	6.55
H-1	3.36 *d* (7)	3.40 *dd* (14, 7.5)	H_A-1	3.37 *dd* (14. 7.5)	3.40 *dd* (14, 7)
		3.32 *dd* (14, 7.5)	H_B-1	3.32 *dd* (14, 7.5)	3.32 *dd* (14, 7)
H-2	5.40 *t* (7.5)	5.39 *t* (7.5)	H-2	5.39 *t* (7.5)	5.41 *t* (7)
H-4	2.18 *d* (7)	2.17 *d* (7)	H-4	2.17 *d* (6.5)	2.18 *d* (6.5)
H-5	4.46 *m*	4.47 *m*	H-5	4.48 *m*	4.49 *m*
H-6	5.12 *d* (8.5)	5.14 *d* (8.5)	H-6	5.16 *d* (8)	5.21 *d* (8)
H-8	2.04 *m*†	1.97 *t* (7)	H-8	1.98 *t* (7)	2.16†
H-9	2.10 *m*†	1.36†	H-9	1.35†	2.36 *m*†
H-10	5.38 *t* (7.5)	1.2 ÷ 1.6†	H-10	1.65†	6.62 *t* (7.5)
H-11	—	2.54 *m*†	H-11	2.71 *m*	—
H-12	4.20 *dd* (8, 5)	—	H-12	—	—
H_A-13	1.87 *m*	2.77 *dd* (18, 6)	H-13	6.37 AB (16)	6.78 AB (16)
H_B-13	1.60†	2.58 *dd* (18, 6)	H-14	6.90	6.81
H-14	2.86 *dd* (7.5, 4.5)	3.09 *t* (6)	H-16	1.34 *s*	1.34 *s*
H-16	1.30 *s*	1.34 *s*	H-17	1.34 *s*	1.34 *s*
H-17	1.26 *s*	1.24 *s*	H-18	1.06 *d* (7)	1.82 *s*
H-18	1.60 *s*	1.07 *d* (7)	H-19	1.62 *s*	1.69 *s*
H-19	1.67 *s*	1.64 *s*	H-20	1.76 *s*	1.77 *s*
H-20	1.77 *s*	1.77 *s*	6′-Me	2.25 *s*	2.26 *s*
6′-Me	2.26 *s*	2.26 *s*	1′-OMe	3.66 *s*	3.67 *s*
1′-OMe	3.67 *s*	3.66 *s*	4′-OMe	3.73 *s*	3.73 *s*
4′-OMe	3.73 *s*	3.73 *s*	-OH	5.10 *s*	—
−OH	6.67 *s*	—			

*Coupling constants (*J* in parentheses) are given in Hz; assignments and chemical shifts of overlapped signals have been obtained by one-bond ^1H–^{13}C correlation spectroscopy.

†Overlapped with other signals.

Me), 2.07 and 1.94 (6H, 2*s*, 2 × MeCOO), 1.75 (3H, *s*, H-20), 1.70 (3H, *s*, H-19), 1.60 (3H, *s*, H-18), 1.23 (6H, 2*s*, H-16 and H-17).

Zosterdiol B (**3**). $[\alpha]_D^{20}$: +1.1° (EtOH; *c* 0.9); IR ν_{max}^{film} cm^{-1}: 3410, 1610, 1485; UV λ_{max}^{EtOH} nm: 222 ($\varepsilon = 12000$), 284 ($\varepsilon = 3000$); HRMS: $[M-H_2O]^+$ 454.3093 (calc. for $C_{29}H_{42}O_4$ 454.3083); MS *m/z* (rel. int.): 454 (2), 436 (2), 366 (3), 285 (9), 271 (6), 253 (8), 243 (5), 235 (5), 220 (49), 205 (35), 189 (22), 187 (18), 175 (12), 167 (22), 165 (100), 151 (16), 147 (13), 145 (11), 137 (14), 135 (45), 121 (9), 119 (9), 105 (14), 91 (13), 81 (9), 43 (7), 41 (10).

Zosteronol (**4**). $[\alpha]_D^{20}$: +1.5° (EtOH; *c* 0.6); IR ν_{max}^{film} cm^{-1}: 3470, 1715, 1610, 1600; UV λ_{max}^{EtOH} nm: 222 ($\varepsilon = 10000$), 282 ($\varepsilon = 2600$); HRMS: $[M-H_2O]^+$ 454.3090 (calc. for $C_{29}H_{42}O_4$ 454.3083); MS *m/z* (rel. int.): 454 (4), 436 (6), 271 (3), 235 (18), 220 (13), 205 (10), 189 (12), 175 (10), 165 (32), 151 (18), 150 (90), 137 (100), 135 (48), 125 (10), 123 (12), 121 (10), 109 (18), 97 (12), 95 (20), 93 (8), 81 (13), 69 (15), 55 (16), 43 (67), 41 (18).

Zosterondiol A (**5**) $[\alpha]_D^{20}$: +0.7° (EtOH; *c* 0.8); IR ν_{max}^{film} cm^{-1}: 3440, 1670, 1630; UV λ_{max}^{EtOH} nm: 222 ($\varepsilon = 18000$), 234 ($\varepsilon = 11700$), 280 ($\varepsilon = 2600$); HRMS: $[M-H_2O]^+$ 454.3088 (calc. for $C_{29}H_{42}O_4$ 454.3083); MS *m/z* (rel. int.): 454 (10), 436 (7), 420 (3), 312 (12), 271 (10), 253 (8), 243 (6), 235 (43), 220 (100), 205 (38), 189 (32), 175 (16), 165 (88), 150 (39), 137 (58), 121 (20), 109 (21), 95 (52), 81 (26), 69 (33), 55 (35), 43 (80), 41 (28).

Zosterondiol A acetate (**6**). Acetylation of **5** gave **6**, oily: IR ν_{max}^{film} cm^{-1}: 3470, 1735, 1610, 1485; ^{1}H NMR: δ6.91 and 6.38 (2H, AB system, $J = 16$ Hz, H-14 and H-13), 6.55 and 6.52 (2H, AB system, $J = 3$ Hz, H-5′ and H-3′), 5.62 (1H, *m*, H-5), 5.34 (1H, *t*, $J = 7.5$ Hz, H-2), 5.10 (1H, *d*, $J = 8$ Hz, H-6), 3.73 (3H, *s*, 4′-OMe), 3.66 (3H, *s*, 1′-OMe), 3.31 (2H, *d*, $J = 7.5$ Hz, H-1), 2.70 (1H, *m*, H-11), 2.26 (3H, *s*, 6′-Me), 1.97 (3H, *s*, MeCOO-), 1.76 (3H, *s*, H-20), 1.63 (3H, *s*, H-19), 1.34 (3H, *s*, H-16), 1.32 (3H, *s*, H-17), 1.07 (3H, *d*, $J = 7$ Hz, H-18).

Zosterondiol B (**7**). $[\alpha]_D^{20}$: +0.9° (EtOH; *c* 0.4); IR ν_{max}^{film} cm^{-1}: 3440, 1665, 1615, 1485; UV λ_{max}^{EtOH} nm: 222 ($\varepsilon = 10800$), 254 ($\varepsilon = 9200$), 284 ($\varepsilon = 2800$); HRMS: $[M-H_2O]^+$ 452.2938 (calc. for $C_{29}H_{40}O_4$ 452.2926); MS *m/z* (rel. int.): 452 (4), 434 (8), 220 (46), 205 (28), 189 (22), 165 (100), 151 (19), 135 (60), 105 (21), 91 (23), 81 (31), 69 (25), 55 (29), 43 (7), 41 (34).

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