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TETRAPRENYLTOLUQUINOLS FROM THE BROWN ALGA *CYSTOSEIRA JABUKAE*

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Key Word Index—*Cystoseira jabukae*, Cystoseiraceae, brown algae, tetraprenyltoluquinols, tetraprenyltoluquinones

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Abstract—The chloroform extract of the brown alga *Cystoseira jabukae* afforded two new tetraprenyltoluquinols and two tetraprenyltoluquinones The structures were determined by spectral analysis and chemical correlations The quinones are possibly artifacts formed by oxidation of the corresponding quinols in the isolation procedure

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INTRODUCTION

The marine genus *Cystoseira* (Phaeophyta) has recently been characterized by the production of tetraprenyltoluquinol derivatives in which a geranylgeranyl side chain has been functionalized in various ways [1–9]

We herein wish to report new representatives of this class of metabolites which have been isolated from *Cystoseira jabukae* Ezgec

RESULTS AND DISCUSSION

Analysis of the chloroform extract of the alga by TLC revealed the presence of two major, and several minor components, which were separated by column chromatography on Florisil

The more polar of the major metabolites, **1**, $C_{27}H_{38}O_4$, was obtained as an optically active clear oil, $[\alpha]_D^{20}$ +8.5°, in 0.09% yield based on the dry weight of the alga extracted The IR spectrum illustrated the presence of hydroxyl (3400 cm^{-1}) and ketone (1705 and 1695 cm^{-1}) functions, while UV absorptions at 219 and 291 nm (ε 12 600 and 4100) were indicative for a hydroquinol chromophore The ^{13}C NMR of **1** (Table 1) contained the appropriate resonances for a disubstituted hydroquinol moiety and in addition revealed the presence of two carbonyls, four *sp*^{2}-hybridized carbons, seven methylenes, two quaternary *sp*^{3}-carbons and six methyl groups These data, together with the molecular formula, required a monocyclic side chain for the metabolite The ^{1}H NMR spectrum showed an AB system (δ6.72 and 6.56, *J* = 3 Hz) assigned to two *meta*-coupled aromatic protons, two further AB system (δ3.18 and 2.99, *J* = 13.5 Hz, δ3.55 and 2.36, *J* = 16 Hz) attributable to isolated methylenes, a methylene doublet (δ3.37, *J* = 7 Hz) coupled with a vinyl proton (δ5.54, *t*, *J* = 7 Hz) which was in turn long range coupled with a broad methyl singlet at δ1.65, a second methylene doublet (δ3.23, *J* = 7.5 Hz) coupled with a vinyl proton (δ5.23, *t*, *J* = 7.5 Hz), and six methyls, three of them on *sp*^{2}-carbons (δ1.76, 1.65 and 1.59, each *s*), two on quaternary *sp*^{3}-carbons (δ0.95 and 1.08, each *s*) and one on an aromatic nucleus (δ2.22, *s*) The rest of the spectrum was a cluster of signals between δ2.1 and 1.3 which were assigned by homonuclear spin decoupling to three contiguous methylenes The above data were interpreted in terms of structure **1**, in which the *E*-geometry of

Table 1 ^{13}C NMR spectral data for compounds **1–4*** (62.9 MHz, CDCl$_3$, TMS as int standard)

C	1	2	3	4
1′	150.3 *s*	187.9 *s*	149.2 *s*	187.5 *s*
2′	136.2 *s*	147.8 *s*	133.8 s^{a}	148.5 *s*
3′	115.3 d^{a}	133.3 d^{a}	115.6 d^{b}	133.2 d^{a}
4′	145.4 *s*	187.9 *s*	152.8 *s*	187.5 *s*
5′	113.1 d^{a}	132.6 d^{a}	112.9 d^{b}	132.3 d^{a}
6′	127.6 s^{b}	145.9 *s*	131.7 s^{a}	145.8 *s*
1	28.3 *t*	27.7 *t*	27.3 *t*	27.6 *t*
2	127.5 *d*	116.3 d^{b}	128.1 *d*	118.1 *d*
3	125.3 s^{b}	135.0 s^{c}	123.6 *s*	134.9 s^{b}
4	56.3 *t*	55.4 *t*	54.6 *t*	39.7 *t*
5	210.1 *s*	208.8 *s*	207.8 *s*	26.5 *t*
6	47.3 *t*	48.3 *t*	47.0 *t*	123.8 *d*
7	45.8 *s*	45.9 *s*	45.8 *s*	139.8 *s*
8	35.8 t^{c}	36.0 t^{d}	35.8 t^{c}	39.7 *t*
9	19.3 *t*	19.3 *t*	19.5 *t*	26.6 *t*
10	33.0 t^{c}	33.1 t^{d}	33.1 t^{c}	124.2 d^{d}
11	60.6 *s*	60.3 *s*	60.8 *s*	134.4 s^{b}
12	217.8 *s*	214.2 *s*	216.8 *s*	39.7 *t*
13	40.9 *t*	40.2 *t*	41.2 *t*	26.8 t^{c}
14	115.6 d^{a}	123.2 d^{b}	115.3 d^{b}	124.4 d^{d}
15	131.5 s^{b}	133.8 s^{c}	136.4 s^{a}	131.1 s^{b}
16	25.6 *q*	25.5 *q*	25.6 *q*	25.6 *q*
17	17.9 *q*	17.9 *q*	17.9 *q*	17.6 *q*
18	21.6 *q*	21.6 *q*	21.8 *q*	16.0 *q*
19	21.4 *q*	21.3 *q*	21.6 *q*	16.0 *q*
20	16.0 *q*	16.4 *q*	15.8 *q*	16.1 *q*
6′-Me	16.0 *q*	15.8 *q*	16.1 *q*	16.1 *q*
OMe	—	—	60.2 *q*	—

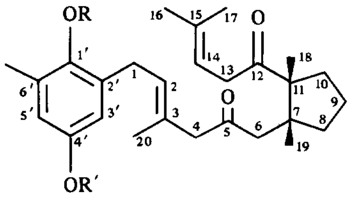
*Multiplicities were obtained by off-resonance decoupling experiments

[a–d] Values with identical superscripts within a column can be interchanged the side-chain double bond at C-2 was deduced from the chemical shift (16 0 ppm) of the vinyl methyl in the ^{13}C NMR spectrum (Table 1) Confirmation of the proposed structure was obtained as follows Dehydration with phosphorus oxychloride of compound **5**, available from previous work [5], gave a mixture of two isomeric compounds (**6** and **7**), $C_{29}H_{42}O_4$, whose structures were evident from their spectral properties (see Experimental), compound **6** was identical in all respects, including the optical rotation, to the methylation product (methyl iodide in the presence of potassium carbonate) of **1** This result in addition assessed the relative stereochemistry of the chiral centres at C-7 and C-11

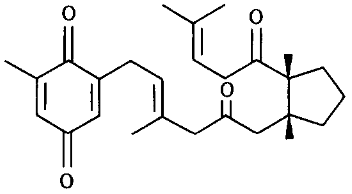
The less polar of the major compounds (**2**), was isolated as a yellow oil, $[\alpha]_D^{20}$ + 9 7°, in 0 03 % yield The molecular formula, $C_{27}H_{36}O_4$, and the spectral characteristics [(IR ν_{max}^{film} 1710, 1695, 1655, 1648 and 1612 cm^{-1}, UV λ_{max}^{EtOH} 254 nm (ε 18 100), ^{13}C NMR and ^{1}H NMR, see Tables 1 and 2] indicated that it was the quinone corresponding to **1** Indeed, silver oxide oxidation of **1** afforded a compound indistinguishable ([α], UV, IR, ^{1}H and ^{13}C NMR) from **2**

One of the minor metabolites of *C jabukae* (**3**, 0 004 % dry wt) had the molecular formula $C_{28}H_{40}O_4$ The ^{1}H NMR spectrum was very similar to that of **1**, the major difference being the presence of a 3H signal at δ3 66, which indicated that one of the hydroxyl groups in toluquinol **1** had become a methoxyl group in **3** Evidence for the position of the methoxyl group at 1′ came from its chemical shift (δ60 2) in the ^{13}C NMR, in closely related compounds OMe groups in positions 1′ or 4′ resonate near 60 and 55 ppm, respectively [10] Partial methylation of **1** with methyl iodide in the presence of potassium carbonate yielded, in addition to **6**, two monomethyl ethers of which the more polar had physical properties identical to those of **3**, while the less polar, **8**, showed in the ^{13}C NMR spectrum a methoxyl resonance at 55 8 ppm

Another of the minor compounds isolated from *C jabukae*, **4**, was an optically inactive liquid, $C_{27}H_{38}O_2$ UV absorptions at 254 nm (ε 16 700) indicated a *p*-



1 $R = R^1 = H$
3 $R = Me$, $R^1 = H$
6 $R = R^1 = Me$
8 $R = H$, $R^1 = Me$



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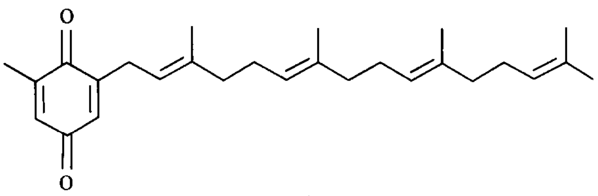

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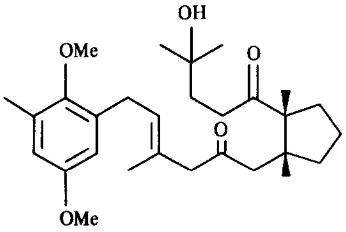

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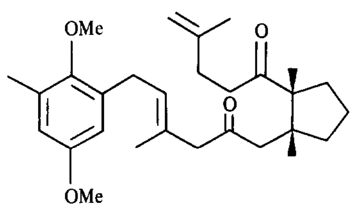

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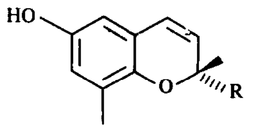

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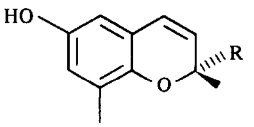

9b

Table 2 ^{1}H NMR spectral data for compounds **1**–**4** (300 MHz, $CDCl_3$, TMS as int standard)

H	**1**	**2**	**3**	H	**4**
3′	6 56 } AB (3)*	6 53 *d* × *t* (2 5, 2)	6 54 } AB (3)	3′	6 44 *d* × *t* (2 5, 2)
5′	6 72	6 56 *d* × *q* (2 5, 2)	6 74	5′	6 52 *d* × *q* (2 5, 2)
1	3 37 *d* (7)	3 19 *d* (7 5)	3 39 *d* (7)	1	3 10 *d* (7 5)
2	5 54 *t* (7)	5 28 *t* (7 5)	5 52 *t* (7)	2	5 14 *t* (7 5)
4	3 18 2 99 } AB (13 5)	3 13 *s*	3 15 2 93 } AB (17)	4 5	1 9–2 1 *m*
6	3 55 2 36 } AB (16)	3 15 2 43 } AB (16)	3 56 2 33 } AB (17)	6	5 08 *m*
8 9 10	1 3, 1 7, 2 1	1 27, 1 7, 2 3	1 3, 1 7, 2 1	8 9	1 9–2 1 *m*
				10	5 08 *m*
13	3 23 *d* (7 5)	3 19 *d* (7)	3 22 *d* (7 5)	12 13	1 9–2 1 *m*
14	5 23 *t* (7 5)	5 28 *t* (7)	5 18 *t* (7 5)	14	5 08 *m*
16	1 76 *s*	1 66 *s*	1 74 *s*	16	1 57 *s*
17	1 59 *s*	1 60 *s*	1 56 *s*	17	1 64 *s*
18	0 95 *s*	0 96 *s*	0 92 *s*	18	1 57 *s*
19	1 08 *s*	1 09 *s*	1 05 *s*	19	1 57 *s*
20	1 65 *s*	1 76 *s*	1 62 *s*	20	1 60 *s*
6′-Me	2 22 *s*	2 07 *d* (2)	2 23 *s*	6′-Me	2 03 *d* (2)
–OMe	—	—	3 66 *s*		

*Coupling constants (*J* in parentheses) are given in Hz, assignments were confirmed by decoupling experiments

benzoquinone moiety, which was confirmed by IR bands at 1650, 1645 and 1610 cm^{-1} In the ^{1}H NMR spectrum H-5′ appeared at δ6 52 as a double quartet (J_d = 2 5 Hz, J_q = 2 Hz), due to long range couplings with H-3′ and 6′-Me, while H-3′ (δ6 44) was a double triplet (J_d = 2 5 Hz, J_t = 2 Hz) coupled with H-5′ and H-1 The latter was in turn vicinally coupled with a vinyl proton at δ5 14 The spectrum also contained resonances from six allylic methylenes (complex multiplet between δ1 9 and 2 1), three vinyl protons (multiplet at δ5 08) and five vinyl methyls (δ1 64, 1 60, 1 57, 1 57 and 1 57, each *s*) From this evidence the compound was formulated as 2′-geranylgeranyl-6′-methylbenzoquinone The ^{13}C NMR spectrum of **4** (Table 1) was in full agreement with the proposed structure and in addition allowed us to assign the *E*-configuration to the internal double bonds of the geranylgeranyl side chain on the basis of the chemical shifts of the pertinent vinyl methyls (*ca* 16 ppm)

Besides the above mentioned compounds, chromatographic separation of the *C jabukae* lipids afforded a fraction homogeneous in TLC which from its ^{1}H NMR spectrum turned out to be a mixture of the isomeric chromenes **9a** and **9b** The most characteristic features of the proton spectrum of this mixture, considered in comparison with that of **1**, was the upfield shift of the aromatic protons (δ6 31 and 6 14, *J* = 3 Hz) and the replacement of the signals pertaining to the benzylic methylene and the adjacent vinyl proton in **1** by an AB system (δ6 09 and 5 61, each *d*, *J* = 9 5 Hz) assignable to the olefin protons at C-1 and C-2 The doublet nature of the signals for the 7-Me and 11-Me revealed that the isolated "compound" was in fact a mixture of two isomers (in approximately equimolar amounts) obviously differing in the stereochemistry at the newly-generated chiral center (C-3) Cyclization of **2** in boiling pyridine afforded a chromene mixture whose ^{1}H NMR was superimposable on that of **9**, which is likely an artifact of the isolation procedure

Finally, it is worth noting that hydroquinone **1** in the course of column chromatography is in part converted into benzoquinone **2**, so it is difficult to assess whether the last compound is really present in the living alga Similarly, quinone **4** could also be an artefact, the natural product being possibly 2′-geranylgeranyl-6′-methylhydroquinol

EXPERIMENTAL

General EIMS (Kratos MS-50 instrument) 70 eV, ^{1}H NMR 300 MHz and 80 MHz, ^{13}C NMR 62 9 MHz All chemical shifts are quoted in ppm (δ) relative to TMS Preparative liquid chromatography (preparative LC) was carried out on a Jobin-Yvon Mini-Prep LC instrument

Plant material Cystoseira jabukae Ezgec (voucher specimen deposited at the Herbarium of the Institute of Botany, Catania, Italy) was collected on rocks at 4–6 m depth in February 1984 at Castelluccio, near Augusta, Sicily

Extraction and purification $CHCl_3$ extraction of the shade-dried and ground alga (100 g) afforded a dark green concentrate (4 g), which was dissolved in hexane and chromatographed on a Florisil column (2 × 50 cm) The polarity of the solvent (hexane) was increased in 10% steps with Et_2O until pure Et_2O was added Fractions of 20 ml were collected and those exhibiting similar TLC profiles were combined

Fraction 10–12 were pooled and subjected to preparative LC (LiChroprep Si-60, 25–40 μm, C_6H_{14}–Et_2O 9 1) to give **4**, oily (3 2 mg, 0 003% dry wt), IR ν_{max}^{film} 1650, 1645, 1610 cm^{-1}, UV λ_{max}^{EtOH} nm (ε) 254 (16 700), HRMS $[M]^+$ 394 2865 (calc for $C_{27}H_{38}O_2$ 394 2871), MS *m/z* (rel int) 396 $[M+2H]^+$ (18), 394 (18), 357 (4), 257 (11), 215 (14), 189 (14), 174 (100), 161 (14), 149 (10), 147 (11), 145 (11), 137 (68), 135 (25), 123 (21), 121 (37), 119 (18), 109 (25), 107 (28), 105 (21), 95 (43), 93 (43), 91 (36), 81 (43), 79 (28), 77 (25), 69 (57), 43 (61), 41 (45)

Fractions 20–25 were combined and purified by preparative LC (C_6H_{14}–Et_2O 4 1) to give pure **3** (4 mg, 0 004% dry wt), $[\alpha]_{20}$ (λ) +8 9° (589), +9 2° (578), +10 6° (546) (*c* 0 9, EtOH); IR ν_{max}^{film} cm^{-1} 3390, 1710, 1690, 1600, UV λ_{max}^{EtOH} nm (ε) 223 (10 900), 285 (2700), HRMS $[M]^+$ 440 2935 (calc for $C_{28}H_{40}O_4$ 440 2926), MS *m/z* (rel int) 440 $[M]^+$ (7), 235 (7), 220 (8), 205 (14), 191 (30), 189 (50), 167 (22), 151 (15), 109 (8), 107 (9), 95 (100), 81 (13), 77 (10), 69 (55), 43 (23), 41 (37)

Fractions 30–38 were pooled and subjected to preparative LC (C_6H_{14}–Et_2O 7 3) to yield pure **2** (30 mg, 0 003% dry wt), $[\alpha]_{20}$ (λ) +9 7° (589), +10 6° (578), +12 2° (546) (*c* 0 9, EtOH), IR ν_{max}^{film} cm^{-1} 1720, 1695, 1655, 1648, 1612, UV λ_{max}^{EtOH} nm (ε) 254 (18 100), HRMS $[M]^+$ 424 2624 (calc for $C_{27}H_{36}O_4$ 424 2613), MS *m/z* (rel int) 426 $[M+2H]^+$ (7), 424 (2), 408 (2), 355 (5), 327 (10), 235 (2), 191 (8), 189 (5), 177 (22), 175 (80), 167 (25), 137 (10), 121 (5), 109 (10), 95 (100), 81 (20), 69 (50), 43 (12), 41 (30) ^{13}C and ^1H NMR see Tables 1 and 2, respectively

Evaporation of fractions 45–57 gave an oily residue (120 mg) which was subjected to preparative LC (C_6H_{14}–Et_2O, 6 4) to give pure **1** (87 mg, 0 09% dry wt), $[\alpha]_{20}$ (λ) +8 5° (589), +9° (578), +9 8° (546) (*c* 2, EtOH), IR ν_{max}^{film} cm^{-1} 3400, 1705, 1695, 1610, UV λ_{max}^{EtOH} nm (ε) 219 (12 600), 291 (4100), HRMS $[M]^+$ 426 2761 (calc for 426 2769), MS *m/z* (rel int) 426 (30), 408 (4), 357 (6), 329 (17), 235 (6), 191 (3), 177 (84), 175 (22), 167 (28), 137 (28), 121 (9), 109 (12), 107 (8), 97 (22), 95 (100), 81 (18), 69 (56), 43 (14), 41 (28) ^{13}C and ^1H NMR see Tables 1 and 2, respectively

Dehydration of **5** *to afford* **6** *and* **7** $POCl_3$ (2 ml) was added to a soln of **5** (100 mg) in C_5H_5N (5 ml) and the mixture was stirred at 0° for 30 min The soln was then diluted with H_2O (5 ml) and extracted with Et_2O Evaporation of the solvent left a residue which was subjected to preparative LC (C_6H_{14}–Et_2O, 22 3) to give **6** (40 mg) and **7** (35 mg)

Compound **6**, oily, $[\alpha]_{20}$ (λ) +18 5° (589), +19 3° (578), +22 4° (546) (*c* 0 6, EtOH), IR ν_{max}^{film} cm^{-1} 1705, 1700, 1595, UV λ_{max}^{EtOH} nm (ε) 215 (11 500), 283 (2900), HRMS $[M]^+$ 454 3091 (calc for $C_{29}H_{42}O_4$ 454 3082), MS *m/z* (rel int) 454 (10), 385 (21), 357 (35), 247 (13), 235 (5), 219 (45), 205 (63), 189 (25), 167 (50), 165 (40), 137 (12), 135 (25), 109 (23), 97 (23), 95 (83), 81 (13), 69 (100), 43 (15), 41 (45), ^1H NMR (80 MHz, $CDCl_3$, TMS) δ6 40 [2H, *s* (*br*), H-3′ and H-5′], 5 27 (1H, *t*, *J* = 7 5 Hz, H-2), 5 16 (1H, *t*, *J* = 7 Hz, H-14), 3 66 and 3 60 (each 3H, each *s*, 2 × OMe), 3 30 (2H, *d*, *J* = 7 5 Hz, H-1), 3 08 (2H, *d*, *J* = 7 Hz, H-13), 3 02 (2H, *s*, H-4), 3 01 (1H) and 2 38 (1H) (AB system, *J* = 16 Hz, H-6), 2 22 (3H, *s*, 6′-Me), 1 72 (6H, *s*, H-17 and H-20), 1 56 (3H, *s*, H-16), 1 04 (3H, *s*, H-19), 0 92 (3H, *s*, H-18)

Compound **7**, oily, $[\alpha]_{20}$ (λ) +21 7° (589), +22 5° (578), +26 3° (546), +45 5° (436), +57° (365) (*c* 0 9, EtOH), IR ν_{max}^{film} cm^{-1} 1710, 1695, 1605, UV λ_{max}^{EtOH} nm (ε) 220 (12 600), 280 (3900), HRMS $[M]^+$ 454 3073 (calc for $C_{29}H_{42}O_4$ 454 3082), MS *m/z* (rel int) 454 (20), 385 (1), 357 (2), 247 (9), 235 (18), 219 (14), 205 (26), 189 (18), 175 (38), 167 (12), 165 (26), 139 (20), 135 (28), 109 (14), 97 (39), 95 (100), 81 (20), 69 (90), 43 (14), 41 (42), ^1H NMR (80 MHz, $CDCl_3$, TMS) δ6 41 [2H, *s* (*br*), H-3′ and H-5′], 5 29 (1H, *t*, *J* = 7 5 Hz, H-2), 4 60 (1H, *s*, H-16a) and 4 55 (1H, *s*, H-16b), 3 65 and 3 59 (each 3H, each *s*, 2 × OMe), 3 31 (2H, *d*, *J* = 7 5 Hz, H-1), 3 02 (2H, *s*, H-4), 3 0 and 2 40 (each 1H, AB system, *J* = 16 Hz, H-6), 3 1–2 2 (4H, *m*, H-13 and H-14), 2 21 (3H, *s*, 6′-Me), 1 69 (6H, *s*, H-17 and H-20), 1 02 (3H, *s*, H-19), 0 91 (3H, *s*, H-18)

Methylation of **1** MeI (0 2 ml) and K_2CO_3 (150 mg) were added to a soln of **1** (10 mg) in Me_2CO (2 ml) and the mixture refluxed for 3 hr The precipitate was filtered off and the soln was evaporated to give an oily residue which was purified by preparative LC (C_6H_{14}–Et_2O, 17 3) thus affording pure **6** (8 mg), identical in all respects ([α], IR, UV, MS, ^1H NMR) to the sample obtained by dehydration of **5** A parallel run in which the reaction time was shortened to 3 hr gave, after LC separation (gradient elution from 15 to 25% Et_2O in C_6H_{14}) **6** (2 3 mg), **3** (2 5 mg) and **8** (2 mg)

Compound **3** had physical properties ([α], IR, UV, MS, ^1H NMR) identical with those of the natural product

Compound **8**, oily, $[\alpha]_{20}$ (λ) +7 9° (589), +8 1 (578), +9 8° (546), IR ν_{max}^{film} cm^{-1} 3350, 1705, 1695, 1600, UV λ_{max}^{EtOH} nm (ε) 215 (9700), 288 (2430), HRMS $[M]^+$ 440 2931 (calc for $C_{28}H_{40}O_4$ 440 2926), MS *m/z* (rel int) 440 (7), 343 (4), 235 (7), 220 (8), 205 (14), 191 (55), 189 (20), 175 (7), 167 (22), 165 (10), 151 (15), 135 (7), 123 (6), 109 (8), 107 (9), 97 (10), 95 (100), 91 (8), 81 (13), 79 (7), 77 (10), 71 (6), 69 (60), 43 (15), 41 (35) ^1H NMR (80 MHz, $CDCl_3$, TMS) δ6 44 [2H, *s* (*br*), H-3′ and H-5′], 5 29 (1H, *t*, *J* = 7 Hz, H-2), 5 20 (1H, *t*, *J* = 7 Hz, H-14), 3 69 (3H, *s*, OMe), 3 29 (2H, *d*, *J* = 7 Hz, H-1), 3 11 (2H, *d*, *J* = 7 Hz, H-13), 3 08 (1H) and 2 33 (1H) (AB system, *J* = 16 Hz, H-6), 3 02 (2H, *s*, H-4), 2 21 (3H, *s*, 6′-Me), 1 74 (6H, *s*, H-17 and H-20), 1 59 (3H, *s*, H-16), 1 04 (3H, *s*, H-19), 0 92 (3H, *s*, H-18) ^{13}C NMR (62 9 MHz, $CDCl_3$, TMS) δ215 8 *s*, 208 6 *s*, 152 8 *s*, 146 8 *s*, 135 8 *s*, 130 5 *s*, 128 1 *s*, 127 1 *d*, 126 3 *s*, 115 5 *d*, 114 7 *d*, 113 6 *d*, 60 7 *s*, 55 8 *q*, 55 5 *t*, 48 3 *t*, 45 8 *s*, 41 4 *t*, 35 8 *t*, 33 2 *t*, 28 9 *t*, 25 5 *q*, 21 8 *q*, 21 7 *q*, 19 3 *t*, 17 9 *q*, 16 1 *q*, 16 0 *q*

Ag_2O *oxidation of* **1** *to produce* **2** Ag_2O (35 mg) and Na_2SO_4 (30 mg) were added to a soln of **1** (25 mg) in Et_2O (1 5 ml) and the suspension was stirred for 20 min The ppt was filtered off and the soln was evaporated to give **2** (20 mg), identified by comparison of the physical properties ([α], IR, UV, MS, ^1H NMR) with those of the product isolated from the alga

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