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A NOVEL ACYLPHLOROGLUCINOL FROM THE BROWN ALGA *ZONARIA TOURNEFORTII*

VINCENZO AMICO, GIOVANNI NICOLOSI, GIOVANNA ORIENTE, MARIO PIATTELLI and CORRADO TRINGALI

Istituto Dipartimentale di Chimica dell'Università di Catania, V. le A. Doria, Catania, Italy

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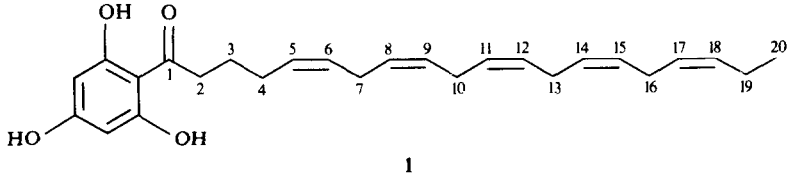
Key Word Index—*Zonaria tournefortii*; Dictyotaceae; brown algae; phloroglucinol derivative; (5*Z*,8*Z*,11*Z*,13*E*,17*Z*)-2′-eicosa-15(*S*)-hydroxy-5,8,11,13,17-pentaenoylphloroglucinol.

Abstract—A novel acylphloroglucinol, (5*Z*,8*Z*,11*Z*,13*E*,17*Z*)-2′-eicosa-15(*S*)-hydroxy-5,8,11,13,17-pentaenoylphloroglucinol, has been isolated from the brown alga *Zonaria tournefortii* and its structure proved by spectroscopic and chemical methods.

In a previous paper [1], we have reported the isolation of the acylphloroglucinol (**1**) from the brown alga *Zonaria tournefortii* (Lamouroux) Montagne. Further investigation of this species has now led to the isolation of the related metabolite (5*Z*,8*Z*,11*Z*,13*E*,17*Z*)-2′-eicosa-15(*S*)-hydroxy-5,8,11,13,17-pentaenoylphloroglucinol (**2**). This compound has been isolated from the alkali-soluble fraction of the chloroform extract of the alga by repeated Si gel chromatography as a dextrorotatory pale yellow oil, $[\alpha]_D^{EtOH} + 8.3°$. Its IR spectrum displayed absorptions due to hydroxyl groups (3300 cm^{-1}) and a hydrogen-bonded carbonyl group (1640 cm^{-1}). A UV band at 287 nm (log $\epsilon = 4.25$) which shifted to 314 nm in base was consistent with an acylphloroglucinol moiety. The mass spectra contained no molecular ion, but the largest observable mass peak occurred at *m/z* 408, $C_{26}H_{32}O_4$ (observed 408.2341, calc. 408.2330). However, the empirical formula $C_{26}H_{34}O_5$ for **2** was obtained from elemental analysis and ^{13}C NMR data. On mild catalytic hydrogenation, **2** gave the known 2′-eicosanoylphloroglucinol (**1**) and in addition the decahydro-derivative **3**, $C_{26}H_{44}O_5$, which indicated the presence of five olefinic groups and an aromatic ring.



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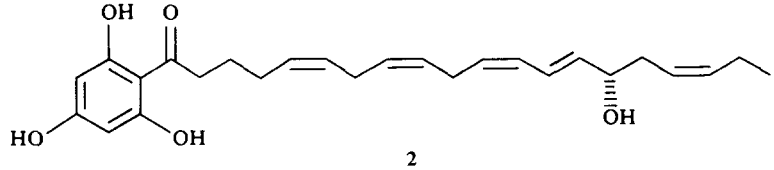

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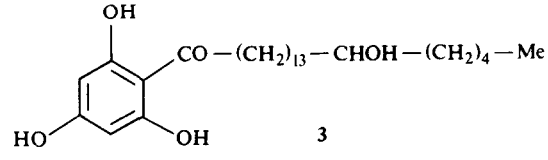

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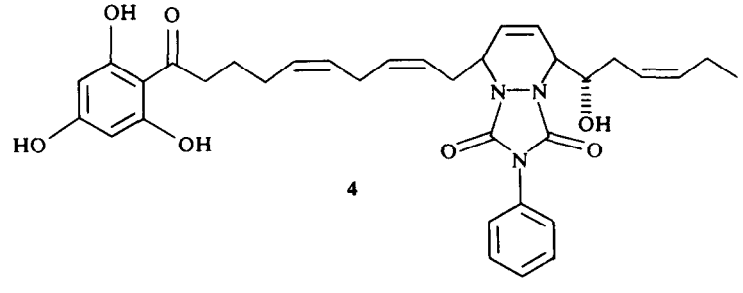

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The ^{13}C NMR spectrum (Table 1) revealed the presence of a phloroglucinol ring [δ 164.21 (2C), 163.31, 105.18 and 96.01 (2C)], a carbonyl group (δ 207.09), ten olefinic carbons (δ 136.04, 134.76, 131.36, 129.90, 129.17, 128.69, 127.96, 127.60, 126.62 and 123.41), seven methylenes (δ 43.36, 35.22, 27.02, 26.24, 25.75, 24.77 and 20.40), a methyl (δ 14.15) and a carbinolic methine (δ 72.82). Analysis of the ^1H NMR spectrum (270 MHz, C_5D_5N, TMS) of **2** (Table 1), including extensive double resonance experiments, showed the presence in the molecule of the partial structures **A–E**. The most notable differences compared with the spectrum of **1** were observed in connection with part structure **D**. The hydroxymethine was seen as a quartet at δ 4.5, and its irradiation modified both the 2H multiplet at δ 2.55 (H_2-16) and the 1H double doublet at δ 5.97 (H-14). Moreover, the former signal was further coupled with the vinyl proton at δ 5.64 (*q*, $J = 8$ Hz, H-17), while the latter was in turn coupled with a triplet at δ 6.10 (H-12), which was also simplified by irradiation at δ 5.44 (H-11). These data showed the presence of a diene system. This was confirmed by reaction of **2** with

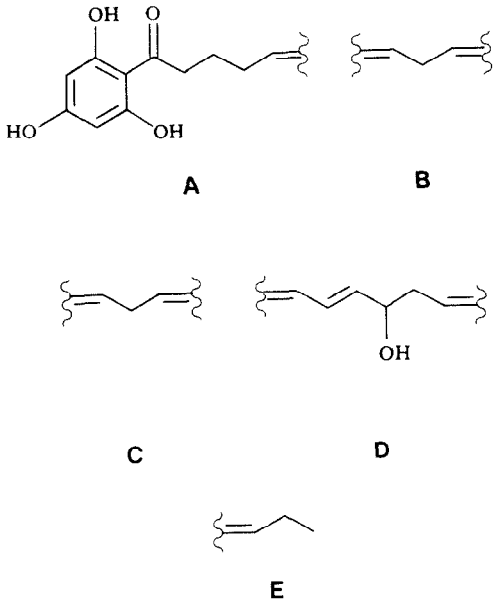

Table 1. ^{13}C and ^1H NMR data for compounds **1** and **2***

Position no.	^{13}C		^1H		
	1†	2	1†	2	DR¶
1′	164.03 *s*	164.21 *s*			
2′	104.94 *s*	105.18 *s*			
3′	164.03 *s*	164.21 *s*			
4′	95.46 *d*	96.01 *d*	6.00 *s*	6.37 *s*	
5′	162.58 *s*	163.31 *s*			
6′	95.46 *d*	96.01 *d*	6.00 *s*	6.37 *s*	
1	206.84 *s*	207.09 *s*			
2	43.35 *t*	43.36 *t*	3.21 *t* (7)	3.37 *t* (7)	*s* {1.93}
3	26.77 *t*	27.02 *t*	1.84 *p* (7)	1.93 *p* (7)	*t* {3.37}, *t*{2.21}
4	24.29 *t*	24.77 *t*	2.19 *q* (7)	2.21 *q* (7)	*d* {1.93}
5	129.71 *d*	129.90 *d*	5.35	5.35–5.44	
6	129.10 *d*	129.17 *d*	5.35		
7	25.56 *t*	25.75 *t*‡	2.85	2.84 *br t*‡	
8	128.74 *d*‡	128.69 *d*	5.35	5.35–5.44	
9	128.07 *d*‡	127.96 *d*	5.35		
10	25.56 *t*	26.24 *t*‡	2.85	2.98 *br t*‡	
11	128.56 *d*‡	126.62 *d*§	5.35	5.44	
12	128.38 *d*‡	134.76 *d*‖	5.35	6.10 *t* (10.5)	*d* {6.85}, *d* {5.44}
13	25.56 *t*	123.41 *d*§	2.85	6.85 *dd* (10.5, 16)	*d* {5.97}, *d* {6.10}
14	128.56 *d*‡	136.04 *d*‖	5.35	5.97 *dd* (6, 16)	*d* {4.50, *d* {6.85}
15	128.38 *d*‡	72.82 *d*	5.35	4.50 *q* (6)	*d* {2.55}, *t* {5.97}
16	25.56 *t*	35.22 *t*	2.85	2.55	{5.64}** {4.50}**
17	127.16 *d*	127.60 *d*§	5.35	5.64 *ddd* (8)	*d* {2.55}
18	132.20 *d*	131.36 *d*	5.35	5.46	
19	20.40 *t*	20.40 *t*	2.07 *p* (7)	2.04 *p* (7)	*d* {0.91}, *q* {5.46}
20	14.87 *q*	14.15 *q*	0.97 *t* (7)	0.91 *t* (7)	*s* {2.04}
OH			9.30	8.00	

*^{13}C NMR: 20.1 MHz, $CDCl_3$, TMS as internal standard, multiplicities were obtained by off-resonance decoupling experiments; ^1H NMR: 270 MHz, C_5D_5N, TMS as internal standard, coupling constants (*J*, Hz) are given in parentheses.

†Included for comparison.

‡, §, ‖ Interchangeable.

¶Signal multiplicity after irradiation at {δ}.

**Simplified.

4-phenyl-1,2,4-triazoline-3,5-dione; the ^{1}H NMR spectra of the two diastereoisomeric adducts (**4**, see Experimental) were very similar and, when compared with that of the parent compound, showed the expected variation of the chemical shifts and multiplicities for the protons of the C-11–C-14 system. Of the six possible structures which can be assembled from fragments **A–E**, only structure **2** was compatible with the MS of the decahydroderivative (**3**) which showed the presence of an ion at *m/z* 365 derived from cleavage of the side chain α to the hydroxyl group.

The *E* configuration of the C-13 double bond was indicated by the value of $J_{13,14}$ (16 Hz), while the *Z* configuration of the double bonds at C-5, C-9 and C-11 was deduced from the chemical shifts observed in the ^{13}C NMR spectrum for the signals of the bisallylic methylenes C-7 and C-10 (δ 25.75 and 26.24); these values were typical for methylenes shielded by two *cis*-double bonds [2]. The *Z* configuration assigned to the double bond at C-17 was inferred from the value of the $J_{17,18}$ (8 Hz) and the chemical shift in the ^{13}C NMR spectrum of the C-19 methylene (δ 20.40), which was identical to that of the pertinent methylene in the spectrum of the (all *Z*)-acylphloroglucinol (**1**). Finally, the stereochemistry of the chiral centre in C-15 was established as *S* by the isolation of *S*-(−)-malic acid from the products of ozonolysis of **2**.

EXPERIMENTAL

Plant material. Z. tournefortii was collected at a depth of 7–10 m near Catania, Sicily, during the summer of 1980. A voucher specimen was deposited in the Herbarium of the Institute of Botany, Catania.

Isolation. The freeze-dried and ground alga (300 g) was extracted (×3) with $CHCl_3$ and the extract was concd under red. pres. to give a dark green residue (11 g) which was taken up in Et_2O. The soln was extracted with 0.2 M NaOH which gave on acidification and extraction into Et_2O 6 g of crude phenolic fraction. Chromatography on Si gel of this fraction with increasing concns of Et_2O in C_6H_{14} gave **1** (0.9 g) and a more polar substance which was rechromatographed on Si gel (CH_2Cl_2–Et_2O, 9 : 1) to give a dextrorotatory pale yellow oil (175 mg) which was homogeneous by TLC. $[\alpha]_D$ +8.3° (EtOH; *c*1); Calc. for $C_{26}H_{34}O_5$, C: 75.21, H: 8.03; Found: C: 73.52, H: 7.98%; UV λ_{max}^{EtOH} nm: 232 (log ϵ 4.57) and 287 (log ϵ 4.25); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3300, 1640–1620, 1450, 1050.

Catalytic hydrogenation of **2**. Compound **2** (10 mg) was hydrogenated at atm. pres. and room temp. in EtOH over 10% Pd–C. The residue obtained after removal of the catalyst by filtration and evaporation of the solvent was chromatographed over Si gel (Et_2O–C_6H_{14}, 2 : 3) to give 4 mg 2′-eicosanoylphloroglucinol, identified by comparison of its physical properties (HPLC, MS) with those of an authentic sample obtained from previous work [1], and 3 mg of **3**, MS *m/z*: 436 $[M]^+$, 418 $[M-H_2O]^+$, 400 $[M-2H_2O]^+$, 365, 318, 293, 181 $[ArCOC_2H_4]^+$, 168 $[ArCOHCH_2]^+$, 153 $(ArCO)^+$.

Reaction of **2** *with* 4-*phenyl*-1,2,4-*triazoline*-3,5-*dione.* Freshly prepared [3] 4-phenyl-1,2,4-triazoline-3,5-dione (20 mg) was added to a soln of 50 mg **2** in 5 ml $CHCl_3$ and the reaction mixture was stirred at room temp. for 5 min. The residue obtained after evapn of the solvent was chromatographed over Si gel (CH_2Cl_2–Et_2O, 7 : 3) to give two diastereoisomeric adducts. The less polar one (6 mg) displayed the following ^{1}H NMR resonances (80 MHz, $CDCl_3$, TMS): δ 7.43 [5H, *s* (*br*) C_6H_5], 6.08 (2H, H-12 and H-13), 5.74 (2H, *s*, H-4′ and H-6′), 5.75–5.25 (6H, H-5, H-6, H-8, H-9, H-17, H-18), 4.69 (1H, H-14), 4.64 (1H, H-11), 4.0 (1H, *q*, J = 6 Hz, H-15), 3.0–2.8 (4H, H_2-7 and H_2-2), 2.7 (2H, *m*, H_2-10), 2.3 (2H, *m*, H_2-16), 2.15 (2H, H_2-4), 2.0 (2H, *m*, H_2-19), 1.73 (2H, *m*, H_2-3), 0.92 (3H, *t*, J = 7 Hz, Me-20). The ^{1}H NMR spectrum of the more polar adduct (5 mg) was very similar, the main difference being observed for the proton at C-15, which appeared as a double doublet (J = 2 and 6 Hz) at δ 4.27.

Ozonolysis of **2**. A soln of **2** (90 mg) in EtOH (5 ml) was cooled to −15° and treated with excess O_3 for 2 hr; 36% H_2O_2 (1 ml) was then added and the mixture refluxed for 2 hr. After addition of H_2O (50 ml) the soln was passed through a column of Dowex 3 (OH^- form) which was eluted with 1 M HCOOH. Evapn of the eluate gave a residue and PC in HCOOH–BuOH–H_2O (1 : 4 : 5) gave 5 mg of laevorotatory malic acid ($[\alpha]_D$ −24°; pyridine).

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