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A PHLOROGLUCINOL DERIVATIVE FROM THE BROWN ALGA *ZONARIA TOURNEFORTII*

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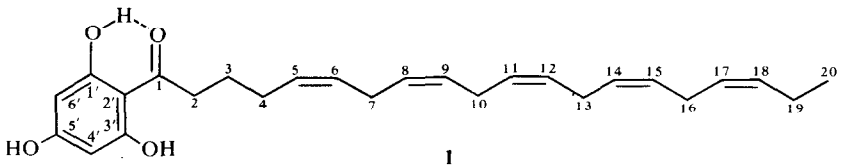
Key Word Index—*Zonaria tournefortii;* Dictyotaceae; brown algae; phloroglucinol derivatives; (all Z)-2′-icosa-5,8,11,14,17-pentaenoylphloroglucinol.

Abstract—The major lipid component of the brown seaweed *Zonaria tournefortii* was identified as the acylphlorogluconol (all *Z*)-2′-icosa-5,8,11,14,17-pentaenoylphloroglucinol.

Zonaria tournefortii (Lamour.) Mont. is a brown seaweed (order Dictyotales) occurring in Mediterranean waters, whose major lipid component is the acylphloroglucinol **1**. This phenol, isolated as an optically inactive oil by Si gel chromatography of the $CHCl_3$ extract of the alga, showed in the IR spectrum absorptions attributable to hydrogen-bonded carbonyl (1640 cm^{-1}) and an OH group (3300 cm^{-1}). The UV spectrum in EtOH exhibited a maximum at 287 nm (log ε 4.09), typical of an acylphloroglucinyl [1], which shifted to 314 nm in base. Mass spectroscopy revealed that the molecular formula was $C_{26}H_{34}O_4$ (*m/z* 410.2439; calcd 410.2451) containing ten double bond equivalents. Mild catalytic hydrogenation of **1** gave a product—**2**, mp 136°; ν_{max}^{KBr} 1650 cm^{-1}, λ_{max}^{EtOH} 288 (log ε 4.27), $C_{26}H_{44}O_4$ (*m/z* 420), which indicated the presence of five reducible double bonds and an aromatic ring. Confirmation of this was obtained from the ^{13}C NMR spectrum of **1** (Table 1) which presented in the sp^2 region, in addition to a carbonyl at 206.84 ppm, resonances at 164.03 (2C), 162.58, 104.94 and 95.46 (2C) attributable to the phenol ring, and at 132.20, 129.71, 129.10, 128.74, 128.56 (2C), 128.38 (2C), 128.07 and 127.16 ppm. Eight methylenes were observable at 43.55, 26.77, 25.56 (4C), 24.29 and 20.40 ppm, and a Me at 14.87 ppm.

Conclusive structural information was obtained from the ^1H NMR spectrum of **1** (Table 1), which displayed a very broad 3 H singlet centred at δ 9.3 (D_2O–exchangeable, –OH), a sharp 2 H singlet at 6.1 (ArH), together with signals due to a non-conjugated pentaene system [$(CH{=}CH{-}CH_2)_4CH{=}CH{-}$ at δ 5.35 (10 H, *m*) and 2.85 (8 H, *m*)]. The spectrum also contained two allylic methylene groups at δ 2.19 (2 H-4, *q*, J = 7 Hz) and 2.07 (2 H-19, *p*, J = 7 Hz), a benzylic methylene group at 3.21 (2 H-2, *t*, J = 7 Hz), a methylene group at 1.84 (2 H-3, *p*, J = 7 Hz) and a methyl triplet at 0.97 (3 H-20, J = 7 Hz). All these assignments were confirmed by decoupling.

The above spectral features were all combined to define the entire structure of the isolated phenol as shown in **1**. The *cis* (*Z*) nature of the double bonds was indicated by the chemical shifts observed in the ^{13}C NMR spectrum for the signals of the four *bis*-allylic methylenes (all at



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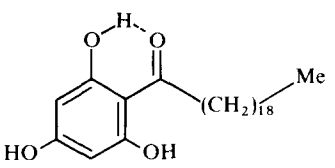

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Table 1. ^{13}C and ^{1}H chemical shifts and multiplicities for compound **1**

Position No.	^{13}C*†	^{1}H†‡	DR§
1′	164.03 (*s*)		
2′	104.94 (*s*)		
3′	164.03 (*s*)		
4′	95.46 (*d*)	6.00 (*s*)	
5′	162.58 (*s*)		
6′	95.46	6.00 (*s*)	
1	206.84 (*s*)		
2	43.35 (*t*)	3.21 (*t*, $J = 7$ Hz)	*s* {1.84}
3	26.77 (*t*)	1.84 (*p*, $J = 7$ Hz)	*t* {3.21}, *t* {2.19}
4	24.29 (*t*)	2.19 (*q*, $J = 7$ Hz)	*d* {1.84}
5	129.71 (*d*)	5.35	
6	129.10 (*d*)	5.35	
7	25.56 (*t*)	2.85	
8	128.74 (*d*)‖	5.35	
9	128.07 (*d*)‖	5.35	
10	25.56 (*t*)	2.85	
11	128.56 (*d*)‖	5.35	
12	128.38 (*d*)‖	5.35	
13	25.56 (*t*)	2.85	
14	128.56 (*d*)‖	5.35	
15	128.38 (*d*)‖	5.35	
16	25.56 (*t*)	2.85	
17	127.16 (*d*)	5.35	
18	132.20 (*d*)	5.35	
19	20.40 (*t*)	2.07 (*p*, $J = 7$ Hz)	*d* {0.97}
20	14.87 (*q*)	0.97 (*t*, $J = 7$ Hz)	*s* {2.07}
OH		9.30	

*Run at 20.1 MHz, $CDCl_3$, TMS; multiplicities were obtained by off-resonance decoupling experiments. Assignments are based on additivity rules and on extrapolation from reported spectra [2, 4, 5].

‡Run at 270 MHz, C_5D_5N, TMS; assignments are based on decoupling experiments and extrapolation from literature data [3, 6].

†Signal multiplicity: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *p* = pentuplet.

§Signal multiplicity after irradiation at {δ}.

‖Interchangeable.

25.56 ppm). Methylene groups shielded by a *trans*- and a *cis*-, or by two *trans*-double bonds resonate downfield from 30 ppm [2].

The MS spectrum of **1** showed a base peak at *m/z* 153 (ArCO) and a series of ions at *m/z* 381, 355, 341, 275, 242, 181 and 168 which can be ascribed to the fragmentation of the methylene-interrupted polyunsaturated side chain.

Some acylphenols, among them a phloroglucinol derivative, have been previously isolated from a brown alga of the family Sargassaceae [3]. To the best of our knowledge, **1** represents the first reported occurrence of a compound of this class in a member of the family Dictyotaceae.

EXPERIMENTAL

Plant material. Zonaria tournefortii (Lamour.) Mont. was collected in June 1979 near Catania, Sicily. A voucher specimen is retained in the Herbarium of the Institute of Botany, Catania.

Isolation. Freeze-dried and ground alga (100 g) was extracted 3 times with $CHCl_3$ and the extract concd under vacuum to leave a dark green oily residue (*ca* 4 g) which was repeatedly chromatographed on a Si gel column with C_6H_{14}–Et_2O mixtures as eluant, yielding **1** (300 mg) as a pale yellow oil, R_f value 0.5 (TLC: C_6H_{14}–Et_2O, 1:1). UV λ_{max}^{EtOH} nm (log ε): 215 (3.97), 226 (3.99), 287 (4.09). IR ν_{max}^{film} cm^{-1}: 3300, 1640, 1620, 1460, 1070, 830, 720.

Catalytic hydrogenation. **1** (114 mg) dissolved in EtOH (5 ml) was hydrogenated in the presence of Pd–C (15 mg) for 20 hr at room temp. and atmospheric pres. Evaporation of the filtered soln gave **2** (110 mg), mp 136° (from EtOH). UV λ_{max}^{EtOH} nm^{-1}: (log ε): 216 (4.11), 226 (4.18), 288 (4.27). IR ν_{max}^{KBr} cm^{-1}: 3400, 1650, 1620, 1470, 820, 730. MS *m/z*: 420 (M^+), 402, 205, 192, 168, 153 (100%), 139, 126. ^1H NMR (270 MHz, C_5D_5N, δ scale): 0.89 (3 H, *br.*, Me), 1.29 (32 H, *m*, C-4–C-19), 1.92 (2 H, pentuplet, $J = 7$ Hz, C-3), 3.44 (2 H, *t*, $J = 7$ Hz, C-2), 6.48 (2 H, *s*, ArH), *ca* 9.5 (3 H, D_2O-exchangeable, OH).

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TWO CINNAMOYL DERIVATIVES FROM *CINNAMOMUM TRIPLINERVIS*

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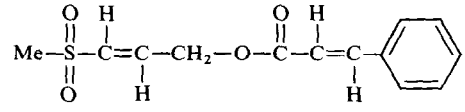
Key Word Index—*Cinnamomum triplinervis*; Lauraceae; cinnamoyl derivatives; *trans*-3-methylsulphonylallyl *trans*-cinnamate; 3-[2-(*trans*-cinnamoylamino)-ethyl]-3-hydroxyindolin-2-one.

Abstract—Two new compounds have been isolated from leaves of *Cinnamomum triplinervis*, the spectroscopic properties of which are in accordance with the structures of *trans*-3-methylsulphonylallyl *trans*-cinnamate and 3-[2-(*trans*-cinnamoylamino)-ethyl]-3-hydroxyindolin-2-one.

High resolution MS revealed the elemental composition $C_{13}H_{14}O_4S$ for compound **1**. In addition to signals for the *trans*-cinnamoyl residue the ^{1}H NMR spectrum shows absorption due to $MeSO_2$ and the *trans*-allyl moiety. Other possible structures are excluded by chemical shift considerations (see refs. [1] and [2]). High resolution electron impact MS (EI), electron addition MS, the UV and IR spectrum are in accordance with structure **1** (see Experimental).

High resolution MS proved the elemental composition to be $C_{19}H_{18}N_2O_3$ for compound **2**. Acid hydrolysis gave the 3-hydroxyindolin-2-one derivative **3** and *trans*-cinnamic acid. The spectroscopic properties of **2** and **3** have been compared with a model compound, 3-hydroxy-3-methylindolin-2-one [3, 4]. This substance and **3** show similar IR and UV spectra (see Experimental). In dilute solution ($CHCl_3$) **2** possesses IR bands at 3586 (OH) and 3434 cm^{-1} (NHCO). Compound **2** and 3-hydroxy-3-methylindolin-2-one show corresponding MS fragments (elimination of O, H_2O, CO, side-chain). Further important fragmentation is indicated schematically in formula **2**. The position, intensity and appearance of the ^{1}H NMR signals for the indolinone part of **2** are in total agreement with those of the aromatic protons of 3-



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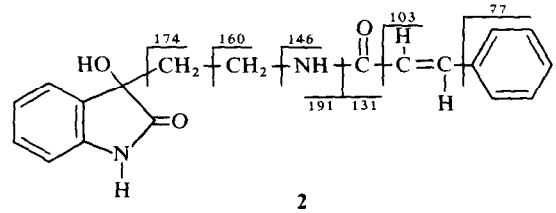

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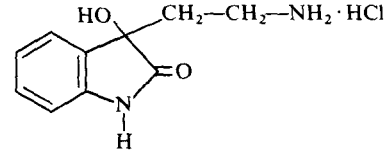

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