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Constituents of *Chondria armata*

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Abstract

A novel long chain fatty ester, pentyl hentriacontanoate **1** and an orange red pigment, caulerpin **2** have been isolated and characterised from a red alga *Chondria armata*. The pigment caulerpin hitherto known to be a constituent of green algae of genus *Caulerpa* is being reported here for the first time from a red alga.

Keywords: *Chondria armata*; Rhodomelaceae; Pentyl hentriacontanoate; Caulerpin

1. Introduction

Red algae of the genus *Chondria* are known for the production of cyclic polysulfides (Wratten and Faulkner, 1976), terpenoids (Fenical and Sims, 1974; Oztunc et al., 1989), novel amino acids (Fattorusso and Piattelli, 1980; Maeda et al., 1986, 1987) and amides (Palermo et al., 1992).

Chondria armata (Kutz.) Okamura, a red alga belonging to Rhodomelaceae, is known to be a source of domoic acid (Daigo, 1959), a proline derivative effective as an anthelmintic. Methanolic extract of this alga exhibited 75% antiviral activity (Kamat et al., 1992) against SFV (Semliki Forest Virus). It is also reported to be hypotensive (Naqvi et al., 1981).

In continuation of our chemical investigation on this alga (Govenkar and Wahidulla, 1999), we have now isolated and characterised two compounds, a fatty acid ester pentyl hentriacontanoate and caulerpin, an orange red pigment, hitherto known to be a constituent of green algae of genus *Caulerpa*.

2. Results and discussion

The ethyl acetate extract (12.3 g) of the alga, *C. armata* (2.5 kg, dry wt) afforded, after repeated chromatography on silica gel, a novel fatty ester, pentyl hentriacontanoate **1** and an orange red pigment caulerpin **2**.

Compound **1**, mp 60–62°C, had IR absorption bands at 2930, 2850 and 730 cm^{-1} for its long aliphatic chain and at 1730 cm^{-1} for the ester carbonyl. Its ^{1}H-NMR displayed a triplet for 6H at δ 0.87 (J = 6 Hz) due to terminal methyls, a downfield triplet at δ 4.05 (J = 6 Hz) was assigned to a methylene adjacent to oxycarbonyl function. A triplet for a methylene adjacent to carbonyl (–CH_2–COO–) was also evident at δ 2.286 (J = 7.5 Hz). A strong broad singlet at δ 1.26 for –$(CH_2)_{28}$– and a signal between δ 1.46–1.6 integrated for 6H attributed to –$(CH_2)_3$– in the esterifying residue were also evident from ^{1}H-NMR.

Its mass spectrum had an $[M]^+$ ion at m/z 536 equivalent to a molecular formula of $C_{36}H_{72}O_2$. A uniform difference of 14 mass units in a large number of fragments in its mass spectrum confirmed the presence of a long aliphatic chain. The absence of an $[M-15]^+$ ion peak indicated a straight chain skeleton (Stoianova-Ivanova and Hadjieva, 1969). The presence of peaks at m/z 129 due to a McLafferty rearrangement and m/z 408 due to the rest of the molecule

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suggested that it is pentyl hentriacontanoate **1**. The fission ions *m/z* 466, 422, 115 and 87 further supported the proposed structure.

The ^{13}C-NMR including DEPT spectra of compound **1** corroborated the presence of an ester carbonyl (δ 174.0), a methylene adjacent to ester carbonyl (δ 34.4) and an oxymethylene at δ 64.4. The remaining methylene signals were observed at δ 31.7, 29.69, 29.27, 29.17, 28.67, 25.91 and 25.04, together with the signals at δ 22.7 and 14.1 due to terminal $-CH_2CH_3$ group. The triplet at δ 29.69 was intense due to the overlapping of equivalent methylenes in the molecule. The NMR spectra of **1** coupled with its mass spectrum confirmed the presence in the molecule of C_{31} straight chain acid moiety with a pentyl group as an ester moiety, thus unequivocally supporting the proposed structure **1**.

Compound **2**, orange red prisms, mp 316–318°C, was identified as caulerpin by comparison of its spectral data with literature values (Santos, 1970; Maiti et al., 1978). However, in ^{1}H-NMR ($CDCl_3$) spectrum of compound **2**, the NH proton resonates much higher at δ 9.2 as compared to δ 11.36 reported for caulerpin in DMSO-d_6. This is expected since in many heterocyclic compounds, more particularly indoles, the chemical shifts of ring protons are susceptible to solvent and concentration changes (Jardine and Brown, 1963; Reinecke et al., 1964). This is attributed to the formation of hydrogen bonds with the solvent molecules (DMSO-d_6), whereas such interactions are negligible when spectrum is taken in $CDCl_3$ (Laszlo, 1964).

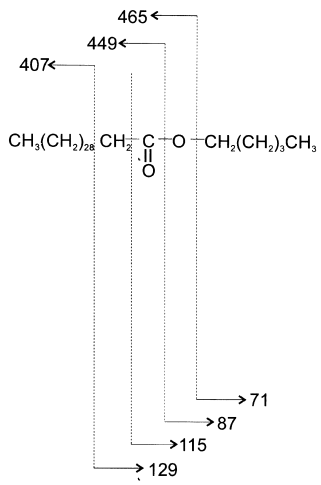
The ^{13}C-NMR data including multiplicities by DEPT of compound **2** is also at variance with those published (Vidal et al., 1984; Anjaneyulu et al., 1991) as evident from Table 1. Hence, final confirmation of identity of compound **2** with caulerpin was established by comparison of its spectral data (^{1}H-, ^{13}C-NMR and DEPT) with the spectral data of a sample of caulerpin isolated from *Caulerpa sertularioides* Gmelin.

Table 1
^{13}C-NMR data of compound **2** and caulerpin **3** ($CDCl_3$)[a]

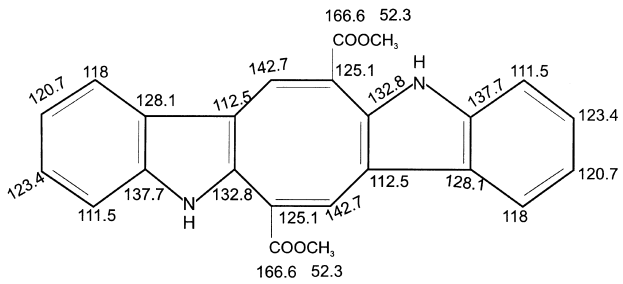
2	3[b]	4[c]	4a[c]
166.65 (*s*)	166.63 (*s*)	165.81 (*s*)	166.7 (*s*)
142.76 (*d*)	142.76 (*d*)	141.58 (*d*)	142.7 (*s*)
137.72 (*s*)	137.69 (*s*)	137.38 (*s*)	138.9 (*s*)
132.88 (*s*)	132.34 (*s*)	137.57	133.5 (*s*)
128.18 (*s*)	128.12 (*s*)	132.91	130.5 (*d*)
125.17 (*s*)	125.41 (*s*)	126.98	128.6 (*s*)
123.39 (*d*)	123.35 (*d*)	125.93	125.0 (*d*)
120.74 (*d*)	120.70 (*d*)	122.93	123.6 (*d*)
118.05 (*d*)	118.02 (*d*)	122.69	121.0 (*d*)
112.50 (*s*)	112.46 (*s*)	117.81	118.0 (*d*)
111.51 (*d*)	111.50 (*d*)	111.19	112.4 (*s*)
52.30 (*q*)	52.49 (*q*)	52.1 (*q*)	51.2 (*q*)

[a] TMS as internal standard, multiplicities by DEPT pulse sequence.
[b] Isolated from *Caulerpa sertularioides*.
[c] Data from Refs. (Vidal et al., 1984; Anjaneyulu et al., 1991) in DMSO.

Caulerpin, a dimer of indole-3-acrylic acid, behaves much like the indole auxins (Schwede et al., 1987). It has not been reported from any other source than the *Caulerpales*. It is physiologically active and toxic to rats and mice (Vidal et al., 1984). It is being reported for the first time from a red alga.



1



3. Experimental

Mps: uncorrected. IR spectrum was recorded in KBr pellet. ^{1}H- and ^{13}C-NMR were obtained in $CDCl_3$ at 300 and 50 MHz, respectively, using TMS as internal standard. EIMS were taken at 70 eV. Silica gel (Merck, 60–120 mesh) was used for column chromatography (CC). Silica gel 60W (Merck) TLC plates were used. Spots were visualised by exposure to I_2 vapours and by spraying with 5% methanolic sulfuric acid followed by heating.

3.1. Collection, extraction and isolation

Chondria armata (2.5 kg) was collected from the west coast of India [15°51′N to 15°54′N and 73°51′E to 73°52′E] at low tides during the pre-monsoon periods, air dried and extracted three times with ethyl acetate. The combined extracts were evaporated under reduced pressure to give a residue (12.3 g) which was chromatographed over silica gel and eluted using mixtures of increasing polarity with ethyl acetate in petroleum ether.

Compound **1**. Fractions 5–15 of the petroleum ether–ethyl acetate (95:5) eluate yielded a residue which on repeated CC gave a white solid (25 mg), mp 60–62°C; R_f = 0.25 (petroleum ether–ethyl acetate, 95:5). IR ν_{max}^{KBr} cm^{-1}: 2929, 2860, 1740, 1440, 1200. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.05 (2H, *t*, *J* = 6.6 Hz, $-OCH_2-$), 2.29 (2H, *t*, *J* = 7.5 Hz, $-CH_2CO-$), 1.60 (6H, *m*, $3CH_2$), 1.26 (56H, *br s*, $28CH_2$), 0.88 (6H, *t*, *J* = 6 Hz, $2CH_3$). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 174 (*s*), 64.4 (*t*), 34.4 (*t*), 29.69–28.67 (*br*), 25.95 (*t*), 25.04 (*t*), 22.70 (*t*), 14.1 (*q*). EIMS (probe) 70 eV, *m*/*z* (rel. int.): 536 $[M]^+$ ($C_{36}H_{72}O_2$, 0.63), 466 (1.8), 436 (15.6), 422 (3.1), 408 (5), 317 (16.9), 298 (20.6), 291 (9.4), 268 (10.6), 253 (56.2), 242 (38.7), 225 (31.3), 211 (100), 209 (85.6), 205 (30), 183 (25.6), 170 (21.3), 151 (25.6), 137 (38.7), 129 (37.5), 123(61.9), 115 (24.4), 109 (98.1), 97 (100), 87 (21.87), 71 (92.5).

Compound **2**. Orange red solid obtained from fractions 16–30 of the petroleum ether–ethyl acetate (4:1) eluate which on repeated CC and recrystallisation from petroleum ether–ethyl acetate afforded orange red prisms (50 mg); mp: 316–318°C; R_f = 0.2 (petroleum ether–ethyl acetate, 4:1). IR ν_{max}^{KBr} cm^{-1}: 3380, 1685, 1260. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.8 (*s*, 6H, 2 × CO_2Me), 7.0–7.4 (8H, *m*, Ar–H), 8.1 (2H, 2 × =CH–) and 9.2 (2H, *s*, 2 × NH). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 166.65 (*s*), 142.76 (*d*), 137.72 (*s*), 132.88 (*s*), 128.18 (*s*), 125.17 (*s*), 123.39 (*d*), 120.74 (*d*), 118.05 (*d*), 112.50 (*s*), 111.51 (*d*), 52.30 (*q*). EIMS (probe) 70 eV, *m*/*z* (rel. int.): 398 $[M]^+$ (39), 366 (6), 306 (12), 279 (37), 251 (9), 199 (10), 57 (100).

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